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Photochemical Oxidants in the Ambient Air of the United States

Environmental Sciences Research Lab.

February 1976

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The problem of photochemical oxidants in the ambient air of the United States is examined with respect to its nature, magnitude, and present day control. Concentration levels of ozone, nitrogen dioxide, peroxyacetyl nitrate, and other photochemically formed pollutants are surveyed, and their effects on human health, vegetation, and materials, as well as their economic impacts, are discussed. Oxidant precursors, hydrocarbons, and nitrogen oxides are reviewed with regard to ambient concentrations and emission rates and in terms of chemical reactions that produce oxidants. Oxidant control efforts are discussed with specific emphasis placed on scientific approaches, emission control methods, costs of control, and control legislation.

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*Concentration (composition)		07D
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CONTENTS

Chapter — Page

LIST OF FIGURES v
LIST OF TABLES. viii
1. INTRODUCTION. 1
References for Chapter 1. 3
2. ATMOSPHERIC LEVELS AND VARIATION OF PHOTOCHEMICAL OXIDANTS. 5
Introduction. 5
Concentrations of Oxidants in Urban Atmospheres 5
Concentrations of Ozone in Urban Atmospheres. 19
Concentrations of Peroxyacetyl Nitrate in Urban Atmospheres 21
Concentrations of Oxidants from Natural Sources 21
References for Chapter 2. 24
3. CHEMISTRY OF OXIDANT FORMATION. 27
Introduction. 27
Mechanism of Oxidant Formation. 27
Hydrocarbon Reactivity. 34
Relationships Between Oxidant and Oxidant Precursors. 43
References for Chapter 3. 55
4. EFFECTS OF METEOROLOGICAL FACTORS ON OXIDANT FORMATION. 59
Introduction. 59
Effects of Sunlight 59
Effects of Temperature and Humidity 61
Transport Phenomena 61
Forecasting Techniques. 63
References for Chapter 4. 65
5. ADVERSE EFFECTS OF OXIDANTS 67
Toxicologic Effects 67
Epidemiological Appraisal of Oxidants 71
Correlation of Oxidant with Eye Irritation. 73
Effects of Oxidants on Vegetation 77
Effects of Oxidants on Materials. 79
References for Chapter 5. 81
6. ATMOSPHERIC LEVELS AND VARIATION OF OXIDANT PRECURSORS AND RELATED POLLUTANTS. 83
Introduction. 83
Concentrations of Hydrocarbons in Urban Atmospheres 83
Concentrations of Nitrogen Oxides in Urban Atmospheres. 94

Chapter | Page

Concentrations of Sulfur Oxides in Urban Atmospheres 111
Concentrations of Aerosols in Urban Atmospheres. 119
References for Chapter 6 124
7. EMISSIONS OF OXIDANT PRECURSORS. 129
Introduction 129
Nationwide Emissions 129
South Coast Air Basin Emissions. 133
References for Chapter 7 137
8. RELATIONSHIPS BETWEEN AIR QUALITY AND EMISSIONS. 139
Introduction 139
Rollback Models. 139
Other Models and Methods 142
Calculation of Control Requirements. 143
References for Chapter 8 145
9. NATIONAL AND REGIONAL POLICIES FOR ABATEMENT OF PHOTOCHEMICAL AIR POLLUTION. 147
History. 147
Present Policies 148
References for Chapter 9 151
10. IMPLEMENTATION OF ABATEMENT POLICIES 153
Status of State Abatement Programs 153
Control of Hydrocarbons and Nitrogen Oxides from Mobile Sources. 154
Control of Organic Emissions from Stationary Sources 157
Control of Nitrogen Oxides from Stationary Sources 160
Estimation of Emission Rates 162
References for Chapter 10. 169
11. ECONOMIC CONSEQUENCES OF OXIDANT POLLUTION 173
Cost of Oxidant Effects. 173
Direct Costs of Abatement. 173
Impact of Abatement on Economy 180
References for Chapter 11. 181
TECHNICAL REPORT DATA AND ABSTRACT. 182

LIST OF FIGURES

Figure		Page
2-1	Monthly Variation of Mean Hourly Oxidant Concentrations for Three Selected Cities.	11
2-2	Monthly Variation of Mean Daily Maximum 1-Hour Average Oxidant Concentrations for Three Selected Cities	11
2-3	Diurnal Variation of Mean Hourly Average Oxidant Concentrations in Los Angeles and St. Louis.	12
2-4	Diurnal Variation of Mean Hourly Average Oxidant Concentrations in Philadelphia, August 6-8, 1966	12
2-5	South (California) Coast Air Basin	13
2-6	Annual and 3-Year Moving Averages of Daily Maximum 1-Hour Oxidant Concentrations in Los Angeles for July through September, 1963-1972	17
2-7	Annual and 3-Year Moving Averages of Daily Maximum 1-Hour Oxidant Concentrations in Azusa, Calif., for July through September, 1963-1972.	17
2-8	Annual and 3-Year Moving Averages of Daily Maximum 1-Hour Concentrations in Riverside, Calif., for July through September, 1963-1972.	17
2-9	Average of Daily Maximum 1-Hour Oxidant Concentrations for Months of August in Azusa, Calif., 1957-1972	18
2-10	Distribution of Average of Daily Maximum 1-Hour Oxidant Concentrations (pphm) in Los Angeles Basin During July through September, 1970-1972	19
2-11	Diurnal Variation of Hourly Ozone Concentrations in Philadelphia and Denver	20
2-12	Variation of Mean 1-Hour Average Oxidant and PAN Concentrations, by Hour of Day, in Downtown Los Angeles, 1965	22
2-13	Variation of Mean 1-Hour Average Oxidant and PAN Concentrations, by Hour of Day, at the University of California at Riverside, September 1966	23
2-14	Monthly Variation of Oxidant and PAN Concentrations at the University of California at Riverside, June 1966-June 1967.	23
3-1	Chemical Changes Occurring During Photoirradiation of Hydrocarbon-Nitrogen Oxide-Air Systems	28
3-2	Flow Diagram for Propylene-Nitrogen Oxide-Ultraviolet Reaction System.	30
3-3	A Lumped Kinetic Mechanism for Photochemical Smog.	31
3-4	Correlation of Solvent Reactivity Data from Battelle, SRI, and Shell Studies.	42
3-5	Maximum Daily 1-Hour-Average Oxidants as a Function of 6 to 9 A.M. Averages of Nonmethane Hydrocarbons at CAMP Stations, June through September, 1966 through 1968, Los Angeles, May through October 1967.	45
3-6	Maximum Daily 1-Hour-Average Oxidant Concentrations as a Function of 6 to 9 A.M. Averages of Total Nitrogen Oxides in Washington, D.C., June through September, 1966 through 1968	46
3-7	Maximum Daily 1-Hour-Average Oxidant Concentrations as a Function of 6 to 9 A.M. Average Total Nitrogen Oxides in Philadelphia, June through September, 1965 through 1968	46

Figure | Page

3-8 Maximum Daily 1-Hour-Average Oxidant Concentrations as a Function of 6 to 9 A.M. Averages of Total Nitrogen Oxides in Denver, June through September, 1965 through 1968 47

3-9 Upper Limit of Maximum Daily 1-Hour-Average Oxidant Concentrations, Calculated Nonmethane Hydrocarbon Concentration of 1.5 ppm C, as a Function of Average Total Nitrogen Oxides from 6 to 9 A.M. at Three Los Angeles Stations, May through October 1967 48

3-10 Nonmethane Hydrocarbon-Oxidant Envelopes Superimposed on Maximum Daily 1-Hour-Average Oxidant Concentrations as a Function of 6 to 9 A.M. Average of Total Nitrogen Oxides in Pasadena, California, May through October 1967 49

3-11 Approximate Isopleths for Selected Upper-Limit Maximum Daily 1-Hour-Average Oxidant Concentrations, as a Function of the 6 to 9 A.M. Averages of Nonmethane Hydrocarbons and Total Nitrogen Oxides in Philadelphia, Pa., Washington, D.C., and Denver, Colo., June through August, 1966 through 1968. 50

3-12 Oxidant Isopleths from Laboratory Experiments Showing Effect of Varying Initial Precursor Hydrocarbon (Propylene) and Nitric Oxide Concentrations on Maximum Ozone Concentrations 51

3-13 Equal Response Lines Representing Combinations of Total Nonmethane Hydrocarbon and Nitrogen Oxide Corresponding to Oxidant and Nitrogen Dioxide Yields Equal to the National Air Quality Standards 54

3-14 Equal Response Lines Representing Combinations of Total Nonmethane Hydrocarbon and Nitrogen Oxide Corresponding to Specific Levels of Maximum Ozone Yields 55

4-1 Diurnal Variation of Mean 1-Hour-Average Oxidant Concentrations at Selected California Sites, October 1965. 62

4-2 Diurnal Variation of Mean 1-Hour-Average Carbon Monoxide Concentrations at Selected California Sites, October 1965 62

5-1 Regression Curves Relating Eye Irritation and Simultaneous Oxidant Concentrations from a Number of Stations in the Los Angeles Area 74

5-2 Variation of Mean Maximum Eye Irritation, as Judged by a Panel of "Experts," with Maximum Oxidant Concentrations, Pasadena, August-November, 1955 74

5-3 Relationship Between Oxidant Concentrations and Eye Discomfort in Los Angeles, October 29 through November 25, 1962. 75

5-4 Mean Index of Eye Irritation Versus Oxidant Concentration. 76

6-1 Concentration Ratios for Nonmethane Hydrocarbons/Methane in Los Angeles (213 Hours During October and November 1964) and Cincinnati (574 Hours During September 1964), with 655 $\mu g/m^3$ (1 ppm) Methane Deducted to Correct for Estimated Background Biospheric Concentration. 85

6-2 Nonmethane Hydrocarbons by Flame Ionization Analyzer, Averaged by Hour of Day over Several Months for Various Cities 89

6-3 Nonmethane Hydrocarbons by Flame Ionization Analyzer Averaged by Hour of Day for Three Los Angeles County Sites, October 1966 through February 1967. 90

6-4 Nonmethane Hydrocarbon Trends in Los Angeles, 1963-1972. 94

6-5 Pollutant Trends for July, August, and September in Los Angeles, 1963-1972. 95

Figure | Page

6-6 Distribution of Total Hydrocarbon Concentrations in the South Coast Air Basin. Average of Daily Maximum 1-Hour Concentrations (ppm C) During July, August, and September, 1970-1972 96

6-7 Frequency Distribution of 3-Hour-Average Concentrations of Nitrogen Oxides at Los Angeles CAMP Station, December 1, 1963, to December 1, 1964 99

6-8 Monthly Average of Nitric Oxide Concentrations in Three Cities, 1969-1972 99

6-9 Monthly Average of Nitrigen Dioxide Concentrations in Three Cities, 1969-1972. 99

6-10 Average Daily 1-Hour Concentrations of Selected Pollutants in Los Angeles, California, July 19, 1965 109

6-11 Diurnal Variation of Nitrogen Dioxide Concentrations at Sites in the United States. 110

6-12 Weekday and Weekend 1-Hour-Average Nitric Oxide Levels in Chicago, Illinois, 1962-1964. 110

6-13 Oxides of Nitrogen Trends in Los Angeles, 1963-1972, 6 to 9 A.M. and Maximum One-Hour Average Concentrations. 114

6-14 Distribution of Oxides of Nitrogen Concentrations in the South Coast Air Basin. Average of Daily Maximum One-Hour Concentrations (pphm) During July, August, and September, 1970-1972 114

6-15 Distribution of Nitrogen Dioxide Concentrations in the South Coast Air Basin. Average of Daily Maximum One-Hour Concentrations (pphm) During July, August, and September, 1970-1972 115

6-16 Diurnal Patterns of Sulfur Dioxide Concentrations (Conductimetric Data Taken in Washington CAMP Station in 1968). 118

6-17 Seasonal Patterns of Sulfur Dioxide Concentrations (Monthly NASN Data for 1964-1971) 118

6-18 Seasonal Patterns of Sulfate Concentrations (Monthly NASN Data for 1957-1970) 120

6-19 Long-Term Pattern of Sulfate Concentrations (Monthly NASN Data for 1957-1970) 120

7-1 Percentage of Emissions from Major Sources in the South Coast Air Basin, 1970. 135

9-1 Organization of the U.S. Environmental Protection Agency (June 1975) . . . 149

LIST OF TABLES

Table Page

2-1 Summary of Maximum Oxidant Concentrations Recorded in Selected Cities, 1964-1967 . . . 7

2-2 Cumulative Frequency Distribution of Hourly Average Oxidant Concentration in Selected Cities, 1964-1965 . . . 8

2-3 Summary of Total Oxidant Concentrations Recorded at Camp Sites, 1964-1972 . . . 9

2-4 Highest Monthly Mean of One-Hour Average Oxidant Concentrations Recorded in Selected Cities, 1964-1965 . . . 10

2-5 Oxidant Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of Daily Maximum One-Hour Oxidant Concentrations for July, August, and September . . . 15

2-6 Oxidant Trends in the South Coast Air Basin, 1963-1972, Annual Averages of Daily Maximum One-Hour Oxidant Concentrations for All Days of the Year . . . 15

2-7 Oxidant Trends in the South Coast Air Basin, 1963-1972, Average of Three Highest One-Hour Oxidant Concentrations for July, August, and September . . . 16

2-8 Oxidant Trends in the South Coast Air Basin, 1963-1972, Number of Hours with Oxidant Concentrations Equal to or Exceeding 20 pphm for July, August, and September . . . 16

3-1 Validation Values of Rate Constants and Their Comparison with the Recommended Values of Investigations . . . 32

3-2 Comparison of Reactivities of Different Types of Organics . . . 36

3-3 Photochemical Reactivities of Hydrocarbons . . . 40

3-4 Reactivities and Classification of Solvents . . . 41

6-1 Some Hydrocarbons Indentified in Ambient Air . . . 42

6-2 Mean of Daily Maximum Hourly Average Total Hydrocarbon Concentrations for 17 California Cities, 1968-1969 . . . 87

6-3 Frequency Distribution Data for 6 to 9 a.m. Nonmethane Hydrocarbon Concentrations at Camp Sites, 1967-1972 . . . 88

6-4 Average Atmospheric Light Hydrocarbon Concentrations, by Hour, Los Angeles and Azusa, September through November, 1967 . . . 91

6-5 Total Hydrocarbon Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of Daily Maximum One-Hour Concentrations for July, August, and September . . . 92

6-6 Total Hydrocarbon Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of 6 to 9 a.m. Daily Average Concentrations for July, August, and September . . . 92

6-7 Total Hydrocarbon Trends in the South Coast Air Basin, 1963-1972, Annual Averages of Daily Maximum One-Hour Concentrations for All Days of the Year . . . 93

6-8 Frequency Distribution Data for 6 to 9 a.m. Nitric Oxide Concentrations at CAMP Sites, 1962-1972 . . . 100

6-9 Frequency Distribution Data for 6 to 9 a.m. Nitrogen Dioxide Concentrations at CAMP Sites, 1962-1972 . . . 102

Table Page

6-10 Nitric Oxide Concentration in California by Averaging Time and Frequency, 1963-1967 104

6-11. Nitrogen Dioxide Concentration in California by Averaging Time and Frequency, 1963-1967 106

6-12 Ambient Nitrogen Dioxide Concentrations in Various Cities in 1972 Measured by Different Methods 108

6-13 Oxides of Nitrogen Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of Daily Maximum One-Hour Concentrations for July, August, and September. 111

6-14 Oxides of Nitrogen Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of 6 to 9 a.m. Daily Average Concentrations for July, August, and September. 111

6-15 Oxides of Nitrogen Trends in the South Coast Air Basin, 1963-1972, Annual Averages of Daily Maximum One-Hour Concentrations for All Days of the Year 112

6-16 Nitrogen Dioxide Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of 6 to 9 a.m. Daily Average Concentrations for July, August, and September. 112

6-17 Nitrogen Dioxide Trends in the South Coast Air Basin, 1963-1972, Three-Month Averages of Daily Maximum One-Hour Concentrations for July, August, and September. 113

6-18 Nitrogen Dioxide Trends in the South Coast Air Basin, 1963-1972, Annual Averages of Daily Maximum One-Hour Concentrations for All Days of the Year 113

6-19 Variation of Oxidant and Precursor Concentrations Within the South Coast Air Basin, July, August, and September, 1970-1972 115

6-20 Cumulative Distribution by Percent of Annual Average Sulfur Dioxide Concentrations, Urban Sites 116

6-21 Cumulative Distribution by Percent of Annual Average Sulfur Dioxide Concentrations, Nonurban Sites 116

6-22 Maximum Concentrations of Sulfur Dioxide for Various Averaging Times at CAMP Sites, 1962-1968 117

6-23 Cumulative Distribution by Percent of Annual Average Sulfate Concentrations, Urban Sites. 119

6-24 Cumulative Distribution by Percent of Annual Average Sulfate Concentrations, Nonurban Sites 119

6-25 Suspended Particle Concentrations (Geometric Mean of Center City Station) in Urban Area, 1961-1965 121

6-26 Distribution of Selected Cities by Population Class and Particle Concentrations 1957-1967 122

6-27 Distribution of Selected Nonurban Monitoring Sites by Category of Urban Proximity, 1957-1967 122

6-28 Quarterly and Annual Size Distribution of Particulate Matter Suspended in Air, 1970 123

6-29 Concentration and Size of Particulate Chemical Constituents in Urban Air. 124

7-1 Estimates of Nationwide Hydrocarbon Emissions by Source Category, 1968 . . 130

7-2 Summary of Hydrocarbon Emissions from 22 Metropolitan Areas in the United States, 1967-1968 131

Table Page

7-3 Percent of Total Area Hydrocarbon Emissions by Source Category, 22 Metropolitan Areas in United States, 1966. 131

7-4 Estimates of Nationwide Nitrogen Oxide Emissions by Source Category, 1968 132

7-5 Percent of Total Area Nitrogen Oxide Emissions by Source Category, 22 Metropolitan Areas in the United States, 1966 133

7-6 South Coast Air Basin, Average Emissions of Contaminants into the Atmosphere, 1970 134

7-7 South Coast Air Basin, Comparison of Stationary and Mobile Sources, 1970 135

7-8 South Coast Air Basin, Hydrocarbon and Nitrogen Oxide Emission Rates, 1960-1970. 136

7-9 South Coast Air Basin, Projected Hydrocarbon and Nitrogen Oxide Emission Rates, 1975-1980 136

8-1 Required Emission Reductions Based on Rollback Model with Various Input Variables. 145

9-1 National Air Quality Standards for Oxidant-Ozone, Nitrogen Dioxdie, and Hydrocarbons 150

10-1 Hydrocarbon and Nitrogen Oxide Emission Standards for New Motor Vehicles and Engines, 1973-1976 155

10-2 Sample Calculation of Gasoline Motor Vehicle Exhaust Emission Factors for Hydrocarbons from Light-Duty Vehicles 165

10-3 Sample Calculation of Weighted Speed Adjustment Factor for Hydrocarbon Exhaust Emissions from Light-Duty Vehicles 165

10-4 Sample Calculation of Gasoline Motor Vehicle Crankcase and Evaporative Emission Factors for Hydrocarbon from Light-Duty Vehicles 166

10-5 Emission Factors for Diesel Engines Emission Factor Rating: B 167

10-6 Emission Factors for Aircraft (lb/engine - LTO cycle and kg/engine - LTO cycle) Emission Factor Rating: A. 168

11-1 Estimated Air Pollution Damage Costs in the United States, 1968 174

11-2 Estimated Air Pollution Damage Costs in the United States for 1968 and 1977 with No Pollution Control 174

11-3 Summary of the United States Air Pollution Damage Cost Ranges for 1970 175

11-4 Federal Transaction Costs Associated with Air Pollution Abatement, 1972. . 175

11-5 Cost of Air Pollution Abatement. 176

11-6 Annualized Unit Cost Increases for Light-Duty Vehicles 177

11-7 Annualized Unit Cost Increases for Heavy-Duty Trucks 178

11-8 Estimates of Annual (Cumulative) Unit Costs of Light-Duty Motor Vehicle Hydrocarbon Emission Control 179

11-9 Estimated Cost Effects of the Clean Air Act for Fiscal Year 1971 180

PHOTOCHEMICAL OXIDANTS IN THE AMBIENT AIR OF THE UNITED STATES

CHAPTER 1

INTRODUCTION

The photochemical oxidants problem has been known to exist in the United States for more than 30 years. First manifestations of the problem occurred in California and included accelerated deterioration of rubber products, damage to vegetation, and eye irritation. Subsequent correlative observations suggested certain adverse effects of photochemical oxidants upon human and animal health. By 1947, the problem of oxidants and other photochemical pollutants, in general, had such dimensions that one state (California) developed and enacted legislation specifically addressed to this problem. While the problem is severest in the southwest edge of California, high levels of oxidants are known to occur in every major urban center in the United States and, through transport, in nonurban areas also.

In this report, an effort is made to (1) present and analyze all evidence attesting to the presence of a photochemical oxidants problem in the United States and (2) present and assess the national effort to alleviate this problem. Because of the early appearance and the severity of this problem in the Los Angeles basin of California, this basin's atmosphere was given by far most of the research attention in the area of photochemical air pollution. For this reason, experiences from the Los Angeles situation constitute the main basis of this report.

Most of the material used in this report was taken from existing reports or documents such as the Air Quality Criteria reports for hydrocarbons, oxidants, and nitrogen oxides[1-3] and the Control Technique documents for hydrocarbon and nitrogen oxide emissions from mobile and stationary sources.[4-6] Such documents present information and viewpoints generated prior to 1970; however, some sections of this report have been more recently updated.

The term "photochemical oxidants" is used by convention to define those atmospheric pollutants that are photochemical reaction products and are capable of oxidizing neutral iodide ions. Extensive research has unequivocally identified several components of the photochemical oxidants mixture. Thus, ambient oxidants are known to consist mainly of ozone, peroxyacetyl nitrate, and nitrogen dioxide and are suspected to include also, in lesser amounts, other peroxyacyl nitrates, hydrogen peroxide, and alkyl hydroperoxides. An important distinction to be made here is that the formation of nitrogen dioxide in ambient air clearly precedes the formation of the other oxidants. For this reason, the relative levels of nitrogen dioxide and of the aggregate of the other oxidants vary considerably during the day, the nitrogen dioxide being invariably the dominant oxidant earlier in the day. Because of this difference in variation pattern and the differences in effects between nitrogen dioxide and the aggregate of the other oxidants, the nitrogen dioxide pollution problem has been treated independently of the other photochemical oxidants problem. Further, because of its predominance among the other non-nitrogen dioxide oxidants, ozone has been singled out and treated as the sole representative of such oxidants and has been given most of the research attention.

Today, photochemical air quality is defined in terms of concentrations of ozone and nitrogen dioxide only. This should not be interpreted to suggest that other photochemical pollutants are thought to be of less concern. Rather, it reflects (1) the fact that the ozone and nitrogen dioxide pollution problems are more easily measured and, hence, more amenable to research than the eye irritation, plant damage, and visibility reduction problems associated with the other pollutants, and (2) the assumption that abatement of the ozone and nitrogen dioxide pollution problems will in all probability alleviate the other photochemical pollution problems also.

The oxidants found in the lower levels of the earth's atmosphere have been traced to both natural and anthropogenic sources. One natural source of oxidants is the abundantly present ozone in the stratosphere, which can be transported into the biosphere. Oxidants can also form naturally from electrical discharges in the atmosphere as well as from atmospheric photochemical reactions involving naturally emitted organic vapors and nitrogen oxides. Obviously, the levels of oxidants resulting from the total of such uncontrollable sources must be known if assessment of the anthropogenic sources is to be made reliably.

Oxidants from anthropogenic sources are products of atmospheric photochemical reactions involving primary organic and inorganic pollutants and atmospheric oxygen. More specifically, the oxidant formation process is initiated by the sunlight-induced photolysis of nitrogen dioxide to nitric oxide and oxygen atoms ($NO_2 \rightarrow NO + O$). Resultant oxygen atoms react then both with atmospheric molecular oxygen to form ozone and with organic pollutants to form other (nonozone) oxidizing species that convert a considerable part of the nitric oxide back into nitrogen dioxide. The net result of this photochemical activity is the accumulation of ozone (and other oxidants) to concentration levels that depend on numerous factors, including local meteorological conditions (sunlight intensity, air stagnation, temperature, etc.) as well as the concentrations, makeup, and variation patterns of the primary pollutants present. Such dependence of oxidant formation on numerous factors makes this pollution problem immensely complex; however, as discussed later, it also has the fortunate consequence that it offers several options to the abatement effort.

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CHAPTER 2. ATMOSPHERIC LEVELS AND VARIATION OF PHOTOCHEMICAL OXIDANTS

INTRODUCTION

Although buildup of photochemical oxidants (OX) occurs in nearly every urban center in the United States, no pollutant episodes involving a sudden and massive assault upon human health have been attributed to photochemical oxidants alone. Accordingly, no case studies in which pollutants and their effects during oxidant pollution episodes were comprehensively and systematically examined have been reported. The case made for viewing the photochemical oxidants as an air pollution problem has been based mainly on (1) observations of humans, animals, plants, and materials in areas known to have high oxidant levels, and (2) results from studies in which human subjects, animals, plants, and materials were deliberately exposed to smoggy atmospheres or to synthetic mixtures containing oxidants. Therefore, in order to present this case, it would be necessary and sufficient to present (1) data on concentration and frequency of occurrence of photochemical oxidants, and (2) evidence regarding the adverse effects of oxidants. Data on the occurrence of oxidants are given in this chapter; evidence on effects of oxidants will be presented and discussed in Chapter 5.

CONCENTRATIONS OF OXIDANTS IN URBAN ATMOSPHERES

Analytical Methods

In the early 1950's, the Los Angeles County Air Pollution Control District (LAAPCD) established the first air monitoring network in the United States (12 stations), using automatic instruments for continuous measurement of gaseous pollutants. Network instrumentation included potassium iodide (KI) total oxidant analyzers; ozone photometers were added in 1958. In 1961, the State of California Department of Public Health organized a 16-station Statewide Cooperative Air Monitoring Network (SCAN). During 1961-1962, the Public Health Service of the U. S. Department of Health, Education, and Welfare initiated its Continuous Air Monitoring Project (CAMP) by installing one CAMP station in each of the following cities: Chicago, Philadelphia, Cincinnati, San Francisco, New Orleans, and Washington (now located in Chicago, Philadelphia, Denver, Cincinnati, St. Louis, and Washington).

Today, data on oxidants are obtained by various techniques in 195 permanent monitoring stations operated by local, state, and Federal agencies. In addition, several temporary stations are being used to obtain data needed for special studies.

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Oxidant has been measured with colorimetric analyzers using neutral-phosphate-buffered 10 percent KI reagent (CAMP, LAAPCD) or 20 percent KI (SCAN). Such analyzers respond not only to ozone (O_3), but also to nitrogen dioxide (NO_2), sulfur dioxide (SO_2), peroxyacetyl nitrate (PAN), and other oxidants. The response to NO_2 is positive and equal to from 10 to 20 percent of that of O_3, depending on the specific analytical procedures used; the response to SO_2 is negative and equal to that of O_3. To eliminate the SO_2 interference, the CAMP analyzers were equipped early in 1964 with chromium trioxide scrubbers, which remove the SO_2 from the sample stream. Therefore, the CAMP oxidant data reported after 1963 were not affected by SO_2 interference. Data reported from all stations, however, are affected by the NO_2 interference.

To adjust the CAMP oxidant data for NO_2, the following equation is used (all concentrations are expressed in parts per million):

$$\text{Adjusted oxidant} = OX - 0.2\ NO_2 \qquad (2\text{-}1)$$

For analyzers equipped with the chromium trioxide scrubber, the data should be additionally adjusted for the NO_2 that results from partial oxidation of nitric oxide (NO) in the chromium trioxide column. Thus, total adjustment is:

$$\text{Adjusted oxidant} = OX - 0.2\ NO_2 - 0.11\ NO \qquad (2\text{-}2)$$

If the oxidant analyzer is not equipped with the chromium trioxide scrubber and the concentration of SO_2 is known, then adjusted oxidant can be computed as follows:

$$\text{Adjusted oxidant} = OX - 0.2\ NO_2 + SO_2 \qquad (2\text{-}3)$$

Such adjusted--otherwise termed here "corrected"--oxidant data represent mainly O_3 and to a lesser degree PAN and other oxidants commonly present in ambient air.

Concentrations

Table 2-1 shows the maximum hourly average concentrations and peak concentrations, as well as the number and percentage of days when the maximum hourly average oxidant concentration exceeded 290, 200, and 100 micrograms per cubic meter ($\mu g/m^3$) (0.15, 0.10, and 0.05 ppm) for 12 monitoring sites.[1] It is interesting to note that peak concentrations in St. Louis reached 1670 $\mu g/m^3$ (0.85 ppm). Such extraordinarily high readings, however, usually occurred at night and were of short duration. It is suspected that the high concentration in St. Louis resulted from emissions from a large chemical complex near the monitor rather than an atmospheric photochemical reaction.

The cumulative frequency distribution of hourly average concentrations for these same 12 sites is presented in Table 2-2. Interpretation of the data in Table 2-2 must be made with caution. For example, on the basis of yearly average, a conclusion that Los Angeles, San Diego, Denver, and Santa Barbara had similar oxidant

Table 2-1. SUMMARY OF MAXIMUM OXIDANT CONCENTRATIONS RECORDED IN SELECTED CITIES, 1964-1967[1]

City	Total days of available data	Number and percent of total days with maximum hourly average ≥ concentration specified						Maximum hourly average, ppm	Peak concentration, ppm
		0.05 ppm		0.10 ppm		0.15 ppm			
		Days	Percent	Days	Percent	Days	Percent		
Pasadena	728	546	75.0	401	55.1	299	41.1	0.46	0.67
Los Angeles	730	540	74.0	354	48.5	220	30.1	0.58	0.65
San Diego	623	440	70.6	130	20.9	35	5.6	0.38	0.46
Denver[a]	285	226	79.3	51	17.9	14	4.9	0.25	0.31
St. Louis	582	362	62.2	59	10.1	14	2.4	0.35	0.85
Philadelphia	556	233	41.9	60	10.9	13	2.3	0.21	0.25
Sacramento	711	443	62.3	104	14.6	16	2.3	0.26	0.45
Cincinnati	613	319	52.0	55	9.0	10	1.6	0.26	0.32
Santa Barbara	723	510	70.5	76	10.5	11	1.5	0.25	0.28
Washington, D.C.	577	313	54.2	65	11.3	7	1.2	0.21	0.24
San Francisco	647	185	28.6	29	4.5	6	0.9	0.18	0.22
Chicago	530	269	50.8	24	4.5	0	0	0.13	0.19

[a] Eleven months of data beginning February 1965.

problems might be reached. Yet examination of the data in Table 2-1 shows that the peak concentration, the maximum hourly average, and the percentage of days with elevated oxidant concentrations are in fact quite different for these four cities. The principal reason for this apparent contradiction is associated with the nature of oxidant formation. Because ozone, the major oxidant, is a photochemical product and not a direct emission, the conditions necessary for its formation are restricted to the hours of sunlight. During any single day, therefore, the time when oxidants can be produced is restricted to a 6- to 8-hour period; at the most, this time interval represents 35 percent of the 24-hour period. On this basis, 65 percent of the cumulative hourly data in Table 2-2 represent values that are close to zero.' As a result, the differences that exist between cities tend to disappear in the process of averaging. Thus, the usefulness and meaning of the yearly averages presented in Table 2-2 have serious limitations.

For similar reasons, the fact that yearly oxidant averages in urban areas approach atmospheric ozone background concentrations has little or no significance. These yearly values are low because 65 percent of the averaged values are necessarily near zero, as previously indicated.

Table 2-2. CUMULATIVE FREQUENCY DISTRIBUTION OF HOURLY AVERAGE OXIDANT CONCENTRATIONS IN SELECTED CITIES, 1964-1965[1] (ppm)

City	Percentile[a]								1964-1965 yearly average
	1	2	5	10	30	50	70	90	
Pasadena	0.26	0.23	0.18	0.12	0.04	0.02	0.01	0.01	0.042
Los Angeles	0.22	0.18	0.14	0.10	0.04	0.02	0.01	0.01	0.036
San Diego	0.14	0.12	0.10	0.08	0.04	0.03	0.02	0.01	0.036
Denver[b]	0.12	0.10	0.08	0.06	0.04	0.03	0.02	0.01	0.036
St. Louis	0.11	0.09	0.07	0.06	0.04	0.03	0.02	0.01	0.031
Philadelphia	0.14	0.11	0.08	0.06	0.03	0.02	0.02	0.01	0.026
Sacramento	0.12	0.10	0.08	0.06	0.04	0.02	0.01	0.01	0.030
Cincinnati	0.10	0.08	0.07	0.06	0.04	0.02	0.02	0.01	0.030
Santa Barbara	0.10	0.09	0.08	0.06	0.04	0.03	0.02	0.02	0.036
Washington, D.C.	0.10	0.09	0.07	0.06	0.03	0.02	0.01	0.01	0.029
San Francisco	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0.01	0.019
Chicago	0.08	0.08	0.06	0.05	0.03	0.02	0.01	0.01	0.028

[a] Concentrations greater than or equal to specified value in indicated percentage of samples.

[b] Eleven months of data beginning February 1965.

Table 2-3 presents, on a yearly basis, the maximum hourly average concentration and the number of days during which the maximum hourly average exceeded specified values for total oxidant at each of the CAMP sites from 1964 through 1972.[2]

Seasonal and Diurnal Variations

Seasonal and diurnal variations in oxidant concentrations result largely from (1) variations in emissions of oxidant-forming pollutants, (2) variations in atmospheric transport and dilution processes, and (3) variations in other atmospheric variables involved in the photochemical formation of oxidant. Typically, each of these factors varies significantly over periods as short as a few hours; the latter two also vary significantly among the seasons. Considerable variations in observed ambient oxidant concentrations, therefore, would be expected.

The highest monthly mean oxidant concentrations generally occur during the period from late spring to early fall. Oxidant concentrations also exhibit a daily variation. For urban centers, the maximum generally occurs around noon, the period when shorter wavelength solar radiation--which is photochemically important--reaches the surface of the earth with greatest intensity. Table 2-4 presents oxidant concentrations recorded in selected cities during the month having the highest mean

Table 2-3. SUMMARY OF TOTAL OXIDANT CONCENTRATIONS RECORDED AT CAMP SITES, 1964-1972[2]

City	Year	Days of valid data	Number of days with at least 1 hourly average ≥ concentration specified			Maximum hourly average, ppm
			0.05 ppm	0.10 ppm	0.15 ppm	
Chicago	1964	254	149	15	0	0.13
	1965	275	120	9	0	0.13
	1966	235	52	6	3	0.19
	1967	255	113	16	1	0.16
	1968	211	113	17	5	0.18
	1969	24	15	0	0	0.07
	1970	200	97	4	3	0.20
	1971	276	90	14	2	0.17
	1972	312	79	4	0	0.14
Cincinnati	1964	303	137	36	5	0.26
	1965	310	182	19	5	0.17
	1966	208	54	1	0	0.10
	1967	228	122	24	1	0.20
	1968	86	65	7	0	0.14
	1969	48	23	5	1	0.16
	1970	7	1	0	0	0.08
	1971	221	96	10	1	0.16
	1972	257	69	3	1	0.15
Denver	1965	285	226	51	14	0.25
	1966	298	187	46	9	0.19
	1967	166	76	12	4	0.21
	1968	151	149	28	5	0.26
	1969	108	70	2	0	0.13
	1970	141	69	9	1	0.18
	1971	184	63	5	1	0.20
	1972	209	94	26	1	0.18
Philadelphia	1964	269	124	37	9	0.20
	1965	266	109	23	4	0.33
	1966	315	145	52	19	0.52
	1967	282	124	28	3	0.17
	1968	140	88	18	3	0.21
	1969	92	37	3	0	0.11
	1970	112	29	10	0	0.13
	1971	260	47	5	0	0.14
	1972	47	20	10	1	0.15
St. Louis	1964	253	156	26	6	0.26
	1965	329	206	33	8	0.35
	1966	292	174	33	5	0.22
	1967	289	185	38	4	0.20
	1968	163	100	7	2	0.23
	1969	95	47	5	0	0.12
	1970	96	20	0	0	0.08
	1971	294	77	1	0	0.13
	1972	203	77	9	2	0.16
Washington, D.C.[a]	1964	293	163	40	4	0.20
	1965	284	150	25	3	0.21
	1966	325	134	27	2	0.16
	1967	322	137	27	5	0.26
	1968	217	134	40	9	0.25
	1969	71	30	1	0	0.10
	1970	167	95	10	2	0.16
	1971	299	144	17	0	0.13
	1972	179	45	6	0	0.13

[a] Site moved at end of 1968.

Table 2-4. HIGHEST MONTHLY MEAN OF ONE-HOUR AVERAGE OXIDANT CONCENTRATIONS RECORDED IN SELECTED CITIES, 1964-1965[1]

City	Month having highest mean 1-hour average oxidant concentration	Monthly mean of hourly average concentrations, ppm	Monthly mean of maximum daily 1-hour average concentrations, ppm
Pasadena	July	0.075	0.24
Los Angeles	August	0.056	0.17
San Diego	October	0.050	0.11
Denver[a]	July[a]	0.050	0.11
St. Louis	May	0.042	0.072
Philadelphia	July	0.054	0.11
Sacramento	June	0.040	0.075
Cincinnati	July	0.048	0.098
Santa Barbara	May and September[b]	0.042[b]	0.064 and 0.072
Washington	May	0.041	0.072
San Francisco	May	0.031	0.046
Chicago	April	0.044	0.070

[a] Eleven months of data beginning February 1965.

[b] 1964-1965 average for the months of May and September.

1-hour average concentration averaged for the years 1964 and 1965. For these months the means of all hourly concentrations and the means of the maximum daily 1-hour average concentrations are listed.

The seasonal variation of oxidant concentrations by month is illustrated in Figures 2-1 and 2-2 for three of the stations. Figure 2-1 illustrates the mean by month of all hourly average concentrations for Los Angeles, Denver, and Phoenix. Figure 2-2 shows the mean by month of daily maximum 1-hour average concentrations for the same cities. In these figures, the importance of solar radiation and temperature--being higher outside the winter season--is readily apparent. Note that for Denver, the high values occur around midsummer. For Los Angeles, the high values occur toward late summer and autumn, apparently reflecting, in part, lower windspeeds and less cloudiness during these seasons. In addition, the characteristics of atmospheric transport in Los Angeles are more favorable to a day-to-day carryover of precursor pollutants in autumn than in midsummer, the result of the greater balance between the sea and land breezes.

In Figure 2-3, the diurnal variation of mean 1-hour average oxidant concentrations are shown for Los Angeles and St. Louis. Selected for the Los Angeles presentation is the calendar month (August) during which the highest monthly mean

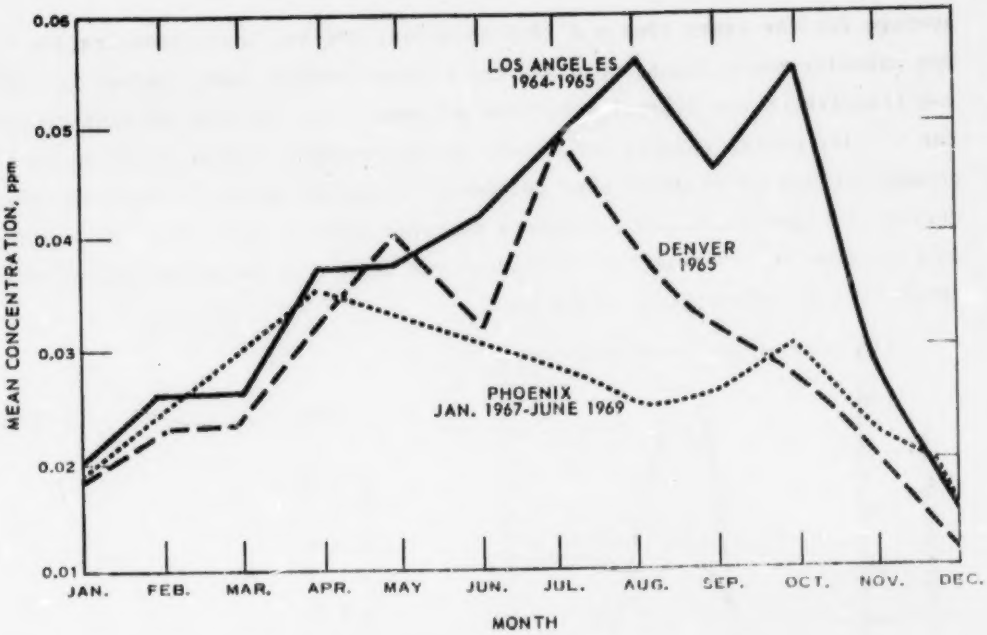

Figure 2-1. Monthly variation of mean hourly oxidant concentrations for three selected cities.[1]

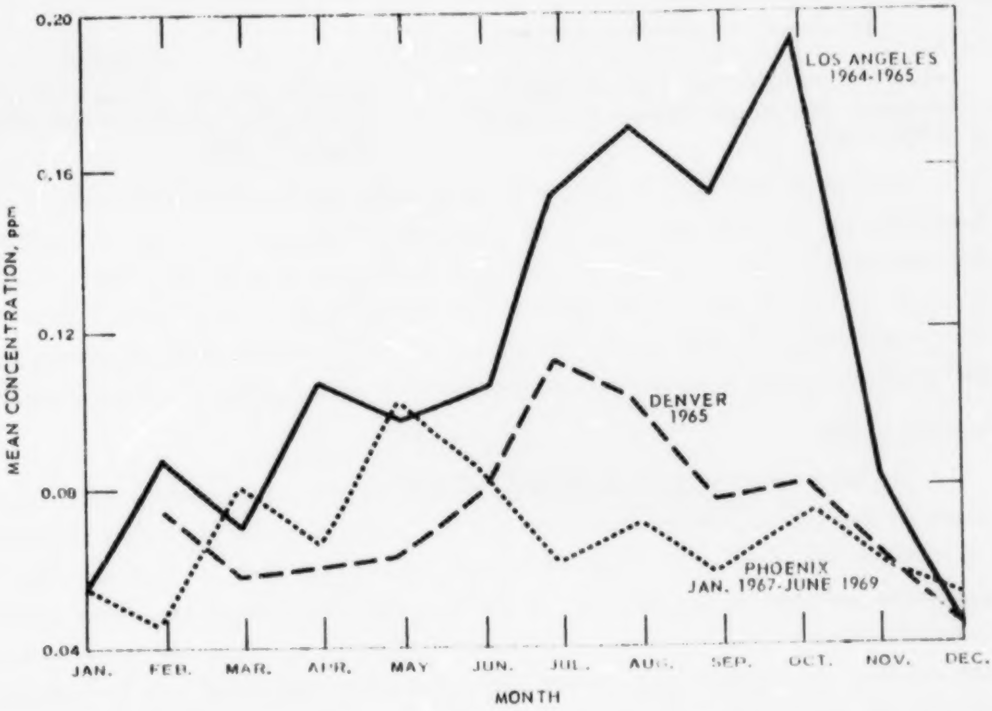

Figure 2-2. Monthly variation of mean daily maximum 1-hour average oxidant concentrations for three selected cities.[1]

average for the years 1964 and 1965 occurred; the St. Louis presentation illustrates the calendar month (June) that had the highest monthly mean average in 1966. Figure 2-4 illustrates the diurnal variation of mean 1-hour average oxidant concentrations for a 3-day period (August 6-8, 1966) in Philadelphia during which unusually high concentrations of oxidants were recorded. Although there are some differences, all curves of Figures 2-3 and 2-4 show a distinct peak around noon. This peak results largely from the interaction of diurnal variations in emissions, solar radiation intensity, and atmospheric dilution.

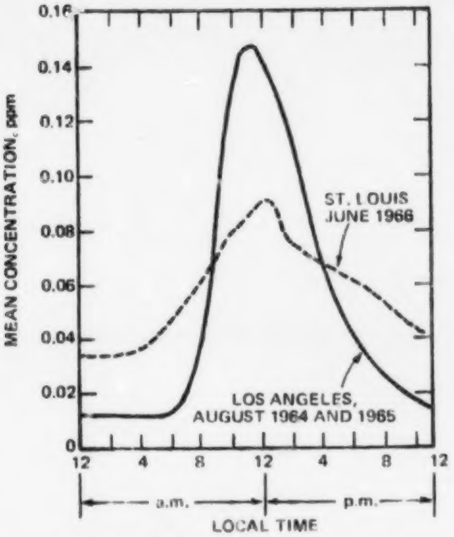

Figure 2-3. Diurnal variation of mean hourly average oxidant concentrations in Los Angeles and St. Louis.[1]

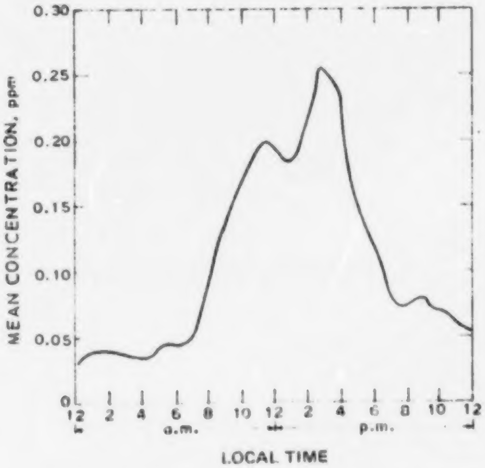

Figure 2-4. Diurnal variation of mean hourly average oxidant concentrations in Philadelphia, August 6-8, 1966.[1]

Peak emissions occur with the morning rush-hour traffic, at a time when solar radiation and dilution are weak. As the vehicle-related emissions drop off toward midmorning and midday, radiation intensity increases to a maximum around noon, dilution increases rapidly in the forenoon to reach a maximum around midafternoon. As a result of these conditions and of the kinetics of the reaction system involved, the diurnal variation of oxidant concentration typically shows a peak around noon.

Oxidant Trends

The most complete data depicting oxidant trends in an urban center are those taken in the Los Angeles basin.[3] The basin, referred to as the South (California) Coast Air Basin, consists of all of Orange and Ventura Counties and the most populated portions of Los Angeles, Riverside, San Bernardino, and Santa Barbara Counties (Figure 2-5).[4] A series of mountain ranges separate the basin from other air basins. In Santa Barbara County, the Santa Ynez Mountains are the approximate separation line. The chain of mountains formed by the San Gabriel, San Bernardino, San Gorgonio, and San Jacinto Mountains separates the basin on the north and east from the Southwest Desert Air Basin.

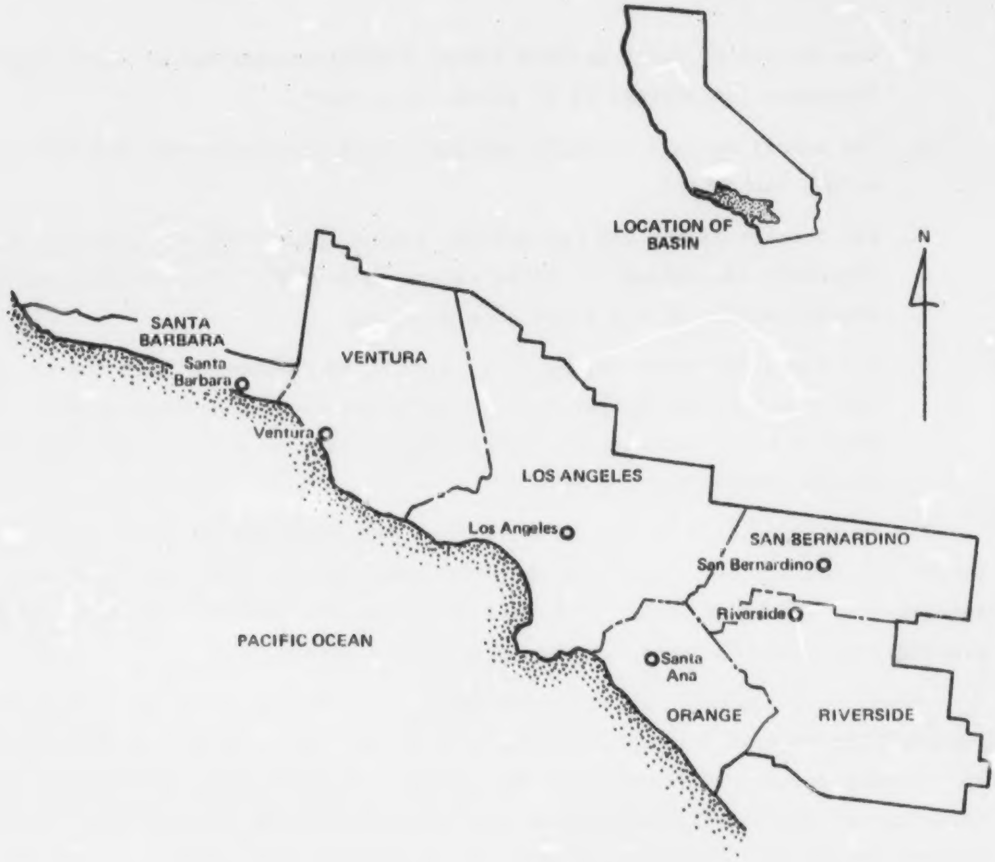

Figure 2-5. South (California) Coast Air Basin.[4]

The basin has an area of approximately 8680 square miles and a population of 9.7 million. Although the basin contains 49 percent of the state's population, it occupies only 6 percent of its area, and population density is 1120 people per square mile. In 1970, there were over 6 million automobiles, trucks, and motorcycles registered in the South Coast Air Basin, an increase of 57 percent since 1960.

During the period 1963-1972, continuous monitoring data were generated by 15 monitoring stations within a 2000-square-mile area within the Los Angeles basin and outlined by the cities of San Bernardino, Azusa, Pasadena, Burbank, West Los Angeles, Lennox, Long Beach, Anaheim, and Riverside. These abundant data are extremely useful not only because they establish reliably the overall oxidant trend in a large population center but also because they help to detect interactions among pollution components in the urban center that cause local oxidant concentrations to deviate from the centerwide trend.

Four methods of data presentation are used here to show the trends of oxidant within the Los Angeles basin:

1. The average of daily maximum 1-hour concentrations during July, August, and September (an average of 92 values each year).
2. The annual average of daily maximum 1-hour concentrations (an average of 365 values each year).
3. The average of the highest maximum 1-hour concentrations in July, August, and September (an average of three values each year). This average represents concentrations on the worst smog days.
4. The number of hours during July, August, and September when the concentrations were equal to or greater than 20 parts per hundred million (pphm). The 20-pphm level is indicative of high smog conditions and has been proposed as a health effect "warning level."

The four types of data for each station, from 1963 through 1972, are shown in Tables 2-5 through 2-8. Data for three stations--Azusa, Riverside, and Los Angeles--are discussed below. The data in Tables 2-5 through 2-8 can be used similarly to show the trends at the other 12 stations.

Based on the data in Tables 2-5 through 2-7, the Azusa air monitoring station recorded the highest oxidant concentrations of any of the stations during most of the 10-year period. Riverside had the greatest increase, and Los Angeles is among those cities whose concentrations have decreased markedly during recent years. The oxidant trends in these three cities are illustrated in Figures 2-6, 2-7, and 2-8, respectively. In these figures, the 3-month (July, August, and September) averages of the maximum 1-hour concentrations are plotted for each year of the 10-year period.

In each of the figures, the annual average of the maximum 1-hour concentration during the smog months varies considerably from year to year. Some of the variability is attributed to the change of emission sources brought about by growth, or by the effect of control programs, and some to changes of locations of the sources. Much of the variability is attributed to meteorological factors. To reduce this latter variability, 3-year moving averages were used as shown in the figures. Each point is plotted at the midyear and represents the average of the July through September maximum 1-hour concentrations during the 3 years. The value of 16 pphm in 1964 in Figure 2-6, for example, is the average during the July-September months of 1963, 1964, and 1965; the point represents the average of 276 measurements.

All of the methods show about the same trends. Perhaps because of the smaller number of measurements, the trends of 3-year averages of the highest three values are not as smooth as the trends of the other averages. It is interesting to observe that all the figures show lower oxidant concentrations at Azusa and Riverside in 1968 than would be expected from the general trend. In the absence of any known changes in emissions in 1968 to account for the decrease, the anomalous concen-

Table 2-5. OXIDANT TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF DAILY MAXIMUM ONE-HOUR OXIDANT CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a],[3]

(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	11.4	9.6	15.9	14.1	12.5	11.9	13.7	10.7	8.9	8.7
Azusa	19.8	24.2	24.4	25.8	26.8	21.9	28.0	28.8	22.9	18.1
Burbank	15.1	15.6	20.9	17.0	22.5	19.0	19.4	18.5	16.1	13.2
Corona	16.4	25.6	16.7	13.8	22.1	16.2	22.0	20.8	13.4	--
La Habra	--	--	15.6	13.3	9.8(2)	11.0	17.2	10.0	15.2	13.3
Lennox	--	--	7.0	7.0	6.7	6.9	6.8	6.2	5.7	3.4
Long Beach	4.2	7.3	6.8	7.8	5.9	4.6	6.3	6.0	6.2	4.0
Los Angeles, Downtown	16.2	15.7	16.2	17.3	13.9	14.3	13.0	13.2	10.0	11.4
Pasadena	20.0	21.9	21.6	22.2	22.6	22.3	27.4	25.7	20.6	17.1
Pomona	--	--	20.8	21.4	23.9	20.8	24.5	23.5	16.6	14.6
Redlands	--	--	--	--	--	17.2	20.4	20.1	17.1	13.6
Reseda	--	--	18.6	19.6	20.9	18.0	20.1	17.4	14.2	12.1
Riverside	17.4	21.2	16.6	18.6	25.2	19.5	25.6	25.6	22.9	22.2
San Bernardino	15.5	12.2	17.0	17.0	18.2	15.2	18.9	23.1	18.7	14.8
West Los Angeles	11.9	10.3	11.3	11.6	11.1	11.2	11.0	10.1	8.4	7.1

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating.

Table 2-6. OXIDANT TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, ANNUAL AVERAGES OF DAILY MAXIMUM ONE-HOUR OXIDANT CONCENTRATIONS FOR ALL DAYS OF THE YEAR[a],[3]

(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	8.0	7.3	11.1	10.1	9.8	8.6	8.6	7.6	6.3	5.9
Azusa	13.2	14.3	15.3	16.1	16.5	14.2	15.2	16.0	13.1	12.0
Burbank	8.9	8.5	12.2	11.5	14.1	12.4	11.3	10.9	9.3	8.6
Corona	13.2(5)	15.6	11.8	9.8	13.8	12.7	12.1	12.3	9.5	--
La Habra	--	--	11.9(1)	9.4	8.1(3)	8.0	9.6(1)	7.4	9.1	8.7
Lennox	--	--	6.4(1)	6.2	6.3	5.5	6.0	5.5	5.1	3.7
Long Beach	4.7	5.3	5.6	5.8	5.0	4.3	4.8	4.4	4.7	4.0
Los Angeles, Downtown	11.2	10.3	11.7	12.0	10.2	9.8	8.8	8.1	7.0	7.6
Pasadena	13.2	13.0	13.7	13.9	14.0	14.4	15.0	15.0	12.0	11.1
Pomona	--	--	16.0(5)	13.9	14.1	13.4	13.0	13.0	9.1	9.5
Redlands	--	--	--	--	5.1(10)	10.0	9.6	10.7	9.1	8.7
Reseda	--	--	13.0(2)	13.0	13.3	10.9	12.0	10.5	9.0	8.3
Riverside	11.5	13.1	10.9	11.3	14.4	12.5	14.2	14.7	13.7	12.2
San Bernardino	9.9	9.9	9.5	11.0	10.7	9.8	9.9	11.8	10.0	8.4
West Los Angeles	9.6	8.0	9.3	9.0	9.8	8.6	8.2	7.5	6.3	5.7

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating.

Table 2-7. OXIDANT TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, AVERAGE OF THREE HIGHEST ONE-HOUR OXIDANT CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a],3

(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	22.3	20.0	33.7	30.3	30.3	27.3	33.3	29.7	27.3	28.7
Azusa	32.3	38.7	44.0	41.7	48.7	38.0	44.7	52.0	40.3	36.0
Burbank	32.7	30.7	35.0	28.0	40.7	36.7	33.0	31.7	27.3	25.0
Corona	32.3	46.0	35.7	29.7	37.7	38.0	40.0	39.7	27.0	--
La Habra	--	--	31.3	26.3	20.0(2)	22.3	39.0	27.0	35.7	32.3
Lennox	--	--	17.7	16.3	15.3	21.3	14.0	12.3	16.3	10.7
Long Beach	13.7	16.0	17.7	18.3	15.0	17.0	14.3	14.7	17.3	13.0
Los Angeles, Downtown	33.7	33.3	29.3	36.0	27.0	37.0	25.0	23.0	19.7	23.7
Pasadena	36.7	36.0	36.7	39.0	36.0	42.0	43.7	45.3	39.7	32.0
Pomona	--	--	37.7	37.3	38.7	41.7	43.3	39.0	33.0	29.3
Redlands	--	--	--	--	--	33.7	35.0	38.3	31.3	26.3
Reseda	--	--	30.0	32.3	34.0	32.3	33.7	33.0	26.0	24.3
Riverside	32.7	39.3	30.0	35.7	44.3	50.0	43.7	53.0	43.3	45.7
San Bernardino	27.3	31.3	34.3	34.3	28.7	27.3	31.3	39.7	30.0	34.0
West Los Angeles	27.3	19.3	22.7	24.0	24.7	24.7	22.7	18.3	17.0	16.0

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating.

Table 2-8. OXIDANT TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, NUMBER OF HOURS WITH OXIDANT CONCENTRATIONS EQUAL TO OR EXCEEDING 20 pphm FOR JULY, AUGUST, AND SEPTEMBER[a],3

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	31	6	61	60	28	18	37	15	12	16
Azusa	108	261	291	303	326	205	318	335	196	116
Burbank	56	58	177	60	206	121	135	97	52	24
Corona	--	--	--	--	--	--	--	--	24	--
La Habra	--	--	--	--	1	15	65	12	62	49
Lennox	--	--	1	3	0	5	0	0	1	0
Long Beach	6	3	2	6	0	2	1	0	1	0
Los Angeles, Downtown	45	48	60	67	31	42	18	15	3	17
Pasadena	167	180	205	159	212	169	313	268	121	66
Pomona	--	--	186	178	251	176	242	207	77	54
Redlands	--	--	--	--	--	124	202	167	96	43
Reseda	--	--	117	112	193	116	167	82	16	15
Riverside	77	174	107	123	301	--	--	--	202	212
San Bernardino	60	69	109	92	123	67	119	231	119	43
West Los Angeles	37	5	15	17	10	19	8	1	2	0

[a] Dashes indicate stations were not operating or data were not reported.

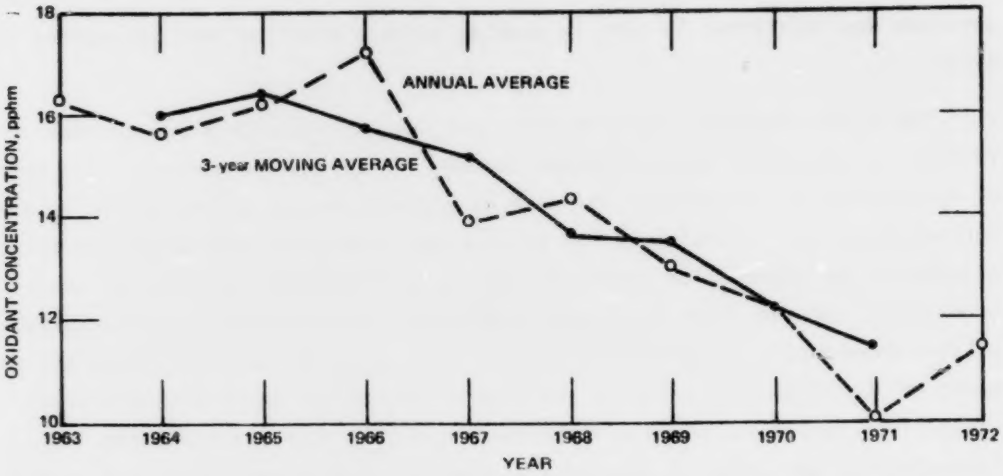

Figure 2-6. Annual and 3-year moving averages of daily maximum 1-hour oxidant concentrations in Los Angeles for July through September, 1963 - 1972.[3]

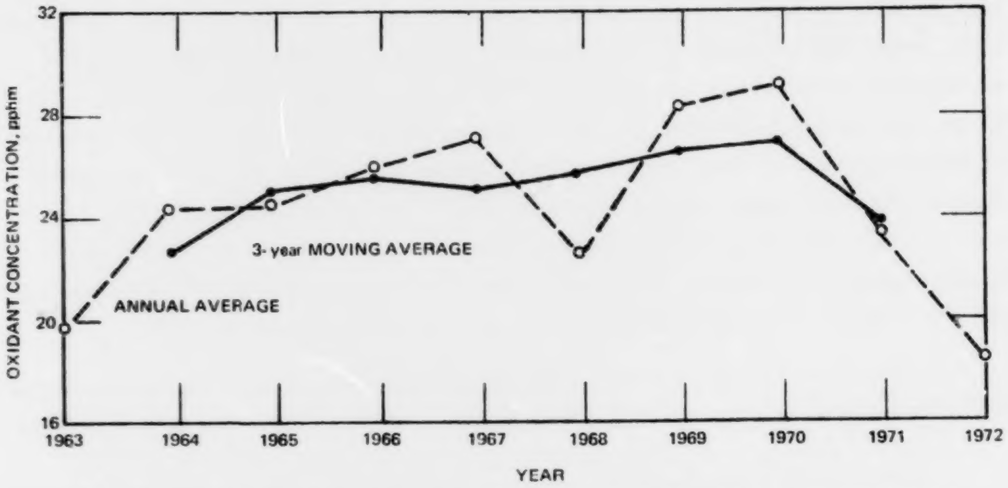

Figure 2-7. Annual and 3-year moving averages of daily maximum 1-hour oxidant concentrations in Azusa, Calif., for July through September, 1963 - 1972.[3]

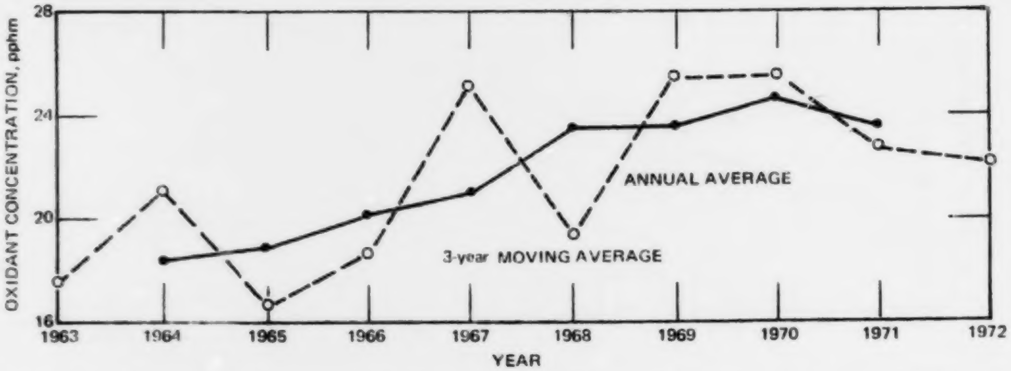

Figure 2-8. Annual and 3-year moving averages of daily maximum 1-hour concentrations in Riverside, Calif., for July through September, 1963-1972.[3]

trations are attributed in part to masking effects from the varying weather conditions.

The 3-year average method reduces, but may not completely remove, measurement variability caused by meteorological factors. A further reduction of the effects of meteorological variability can also be accomplished by adjusting the oxidant concentration for variation in one or more meteorological parameters, if these parameters are known. One parameter that is an important indicator of weather conditions, and for which there were sufficient data available, is the temperature aloft. Examination of such temperature-oxidant data for the Azusa area for the month of August each year during the period 1957-1970 indicated that oxidant concentrations tended to increase approximately 1 pphm for each additional degree Fahrenheit in the value of the monthly average maximum temperature. Evidently then, a basis exists for adjusting the observed oxidant concentrations to remove some of the variability that may be attributed to meteorological conditions. Such adjustment results in lowering the oxidant concentrations for Augusts that were hotter than normal and increasing the concentrations during cooler Augusts. These adjusted concentrations are shown in Figure 2-9; a linear regression line is fitted to the points for 1957 through 1970. The slope of this line and the distribution of points around it lend considerable credence to the existence of an annual increase of 0.64 pphm between 1957 and 1970. The adjusted concentrations for 1971 and 1972 are far below the regression line extrapolated through these years. The abrupt departure from the long-term trend line is of such magnitude as to indicate that the upward oxidant trend at Azusa may have terminated in 1970.

In contrast to Figure 2-7, which showed the 1968 average to be substantially below the 3-year moving average line, Figure 2-9 shows that the adjusted 1968

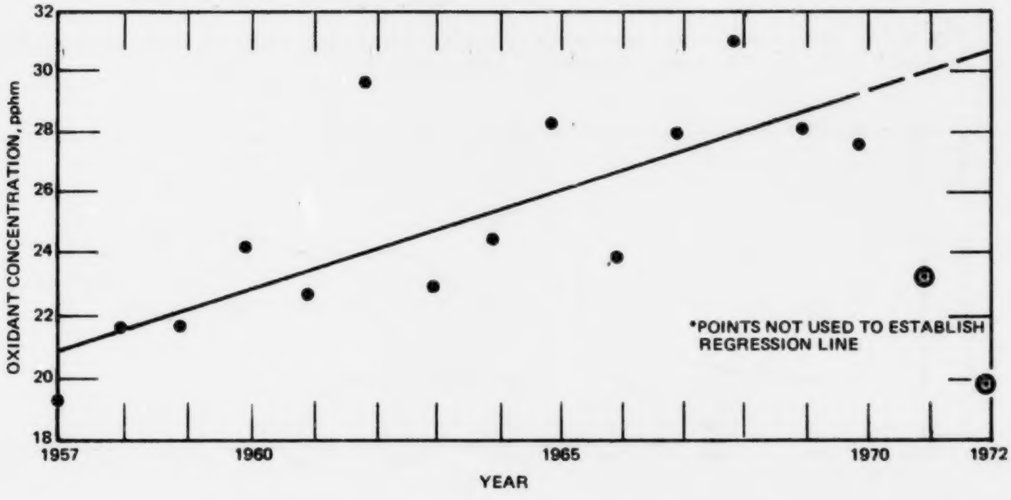

Figure 2-9. Average of daily maximum 1-hour oxidant concentrations for months of August in Azusa, Calif., 1957-1972.[3] (Adjusted for temperature aloft.)

concentration is above the regression line. This supports the premise that in Azusa the low oxidant concentrations in 1968 were caused by weather; whereas the concentrations observed in 1970 and 1971 were not. In Riverside, the 1971-1972 temperature-adjusted concentrations were less than those for the previous 4 years, but the differences did not meet the test for significance at the 5 percent level. Thus, it is not certain whether the concentrations at Riverside peaked in 1970.

The basinwide pattern of oxidant concentrations is readily apparent when the 3-year averages are plotted on a map, as in Figure 2-10. The averages of the maximum 1-hour concentrations in July, August, and September of the latest 3-year period (1970-1972), are shown at each station, and isopleths were drawn for the air basin. Oxidant concentrations are lowest in the southwest, increase steadily toward the northeast, and reach a maximum in the Azusa-Riverside area. Concentrations in Azusa and Riverside are nearly five times higher than in the coastal cities of Lennox and Long Beach.

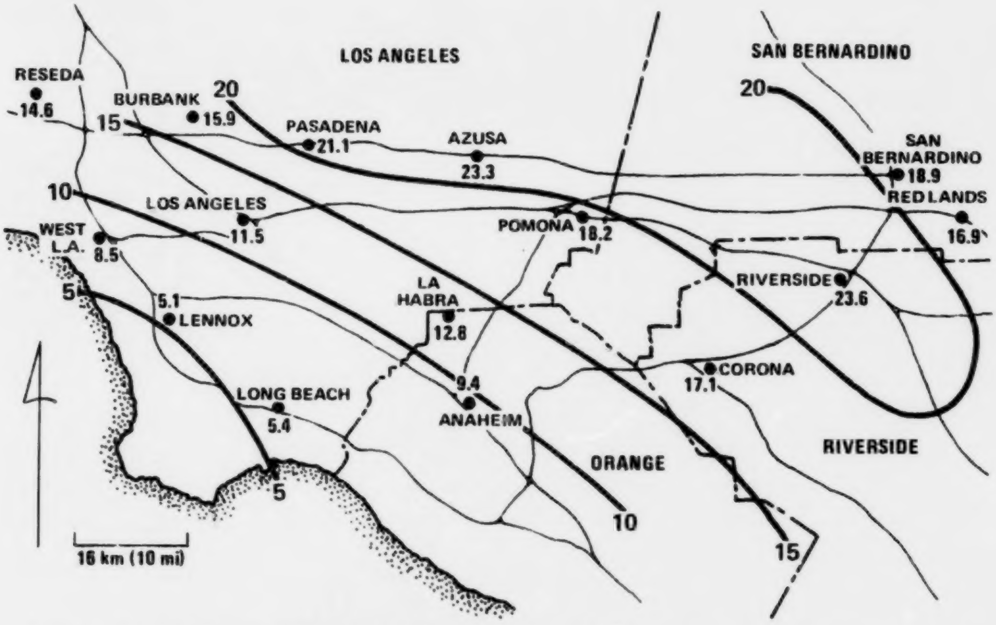

Figure 2-10. Distribution of average of daily maximum 1-hour oxidant concentrations (pphm) in Los Angeles basin during July through September, 1970-1972.[3]

CONCENTRATIONS OF OZONE IN URBAN ATMOSPHERES

In one study, conducted by EPA in the summer of 1971, ambient air measurements were made in several cities using a chemiluminescent detector that responds specifically to ozone.[5] Resultant data are summarized in Table 2-9.

Figure 2-11 shows the diurnal pattern of 1-hour average ozone concentrations measured on 2 selected days at the Denver and Philadelphia CAMP sites. Because the

Table 2-9. SUMMARY OF OZONE MEASUREMENTS IN VARIOUS CITIES, SUMMER 1971[5]

State	City	No. of hourly observations	No. of times standard (0.08 ppm) exceeded	Two highest levels	
Florida	Jacksonville	2044	6	0.100	0.100
	Miami	2092	0	0.050	0.050
	Tampa	1919	0	0.070	0.065
Hawaii	Honolulu	1388	0	0.024	0.023
Indiana	Indianapolis	2070	74	0.140	0.130
Iowa	Des Moines	2141	17	0.105	0.100
Kansas	Wichita	2536	4	0.105	0.095
Kentucky	Louisville	1836	74	0.140	0.140
Louisiana	New Orleans	2289	58	0.130	0.125
Minnesota	Minneapolis	2025	1	0.095	0.080
Nebraska	Omaha	2073	1	0.090	0.075
New Mexico	Albuquerque	2209	8	0.115	0.095
New York	Rochester	2391	110	0.155	0.150
North Carolina	Charlotte	2097	38	0.109	0.106
Ohio	Cleveland	1886	23	0.145	0.125
	Columbus	2214	112	0.145	0.130
	Dayton	2395	168	0.190	0.175
	Toledo	2342	156	0.156	0.140
Oklahoma	Oklahoma City	1684	32	0.135	0.120
	Tulsa	2113	18	0.115	0.115
Pennsylvania	Pittsburgh	2629	105	0.165	0.155
Puerto Rico	San Juan	1177	0	0.055	0.045
Tennessee	Memphis	1644	34	0.140	0.130
	Nashville	1713	13	0.115	0.115
Texas	Austin	2134	14	0.150	0.110
	Corpus Christi	2263	59	0.190	0.185
	Dallas	2125	38	0.135	0.125
	El Paso	2775	6	0.130	0.120
	Houston	2583	48	0.155	0.150
	San Antonio	1919	55	0.145	0.145
Virginia	Norfolk	1638	9	0.105	0.105
	Richmond	1353	33	0.117	0.112
Wisconsin	Milwaukee	2296	64	0.190	0.170

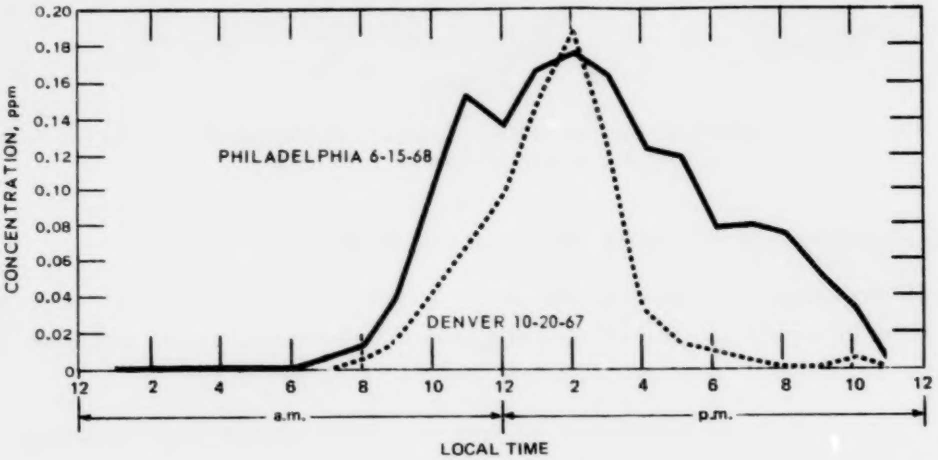

Figure 2-11. Diurnal variation of hourly ozone concentrations in Philadelphia and Denver.[2]

analytical method for ozone is relatively new, ambient ozone data accumulated thus far are sketchy.

CONCENTRATIONS OF PEROXYACETYL NITRATE IN URBAN ATMOSPHERES

Peroxyacetyl nitrate concentrations were measured in Los Angeles using gas chromatographic techniques with an electron-capture detector during September and October 1965.[6] Seven measurements per day were made for each of 16 weekdays in September and 19 weekdays in October. The mean 1-hour-average concentrations of PAN and oxidant by hour of day for these periods are shown in Figure 2-12.

Beginning in June 1966, measurements of PAN have been made on the campus of the University of California at Riverside, also with the gas chromatograph and electron-capture detector.[1] Samples are usually collected once each hour between 6 a.m. and 5 p.m. In Figure 2-13, the mean 1-hour-average oxidant concentrations, as measured with a Mast analyzer, and the mean 1-hour-average PAN concentrations are shown by the hour of the day for the month of September 1966. The monthly mean hourly oxidant and PAN concentrations and the monthly mean of the daily maximum hourly average of 1 year's data are shown by month in Figure 2-14.

The comparison shown in Figure 2-14 is a good illustration of how specific averaging processes affect results. The considerable variations in daily maximum hourly concentrations as a function of time of year become much less obvious if the data include all hours. As stated previously, the latter dampening effect is the result of including in the data those hours for which oxidant is necessarily at or near zero. Because these near-zero hours account for approximately 65 percent of the time of sampling, they have the effect of averaging-out the elevated daytime values. Each method of averaging has its purpose, however, and subsequent interpretations of the results require careful consideration.

In Figure 2-13, there are two daily maxima for the oxidant and PAN concentrations. The PAN concentrations in Riverside are an order of magnitude lower than those in Los Angeles; the concentrations of oxidants are of the same order of magnitude.

CONCENTRATIONS OF OXIDANTS FROM NATURAL SOURCES

Natural sources of the oxidants found in the lower atmosphere include electrical discharges, stratospheric ozone, and atmospheric reactions of naturally emitted organics and nitrogen oxides. Of these, the electrical discharge source is believed to contribute only negligibly to biospheric ozone.

Stratospheric ozone, formed by the action of solar radiation upon oxygen at altitudes between 15 and 37 kilometers can contaminate the lower atmospheric layers through vertical transport. Although several theories are available to explain the manner in which such transport occurs, it is generally believed that--with the

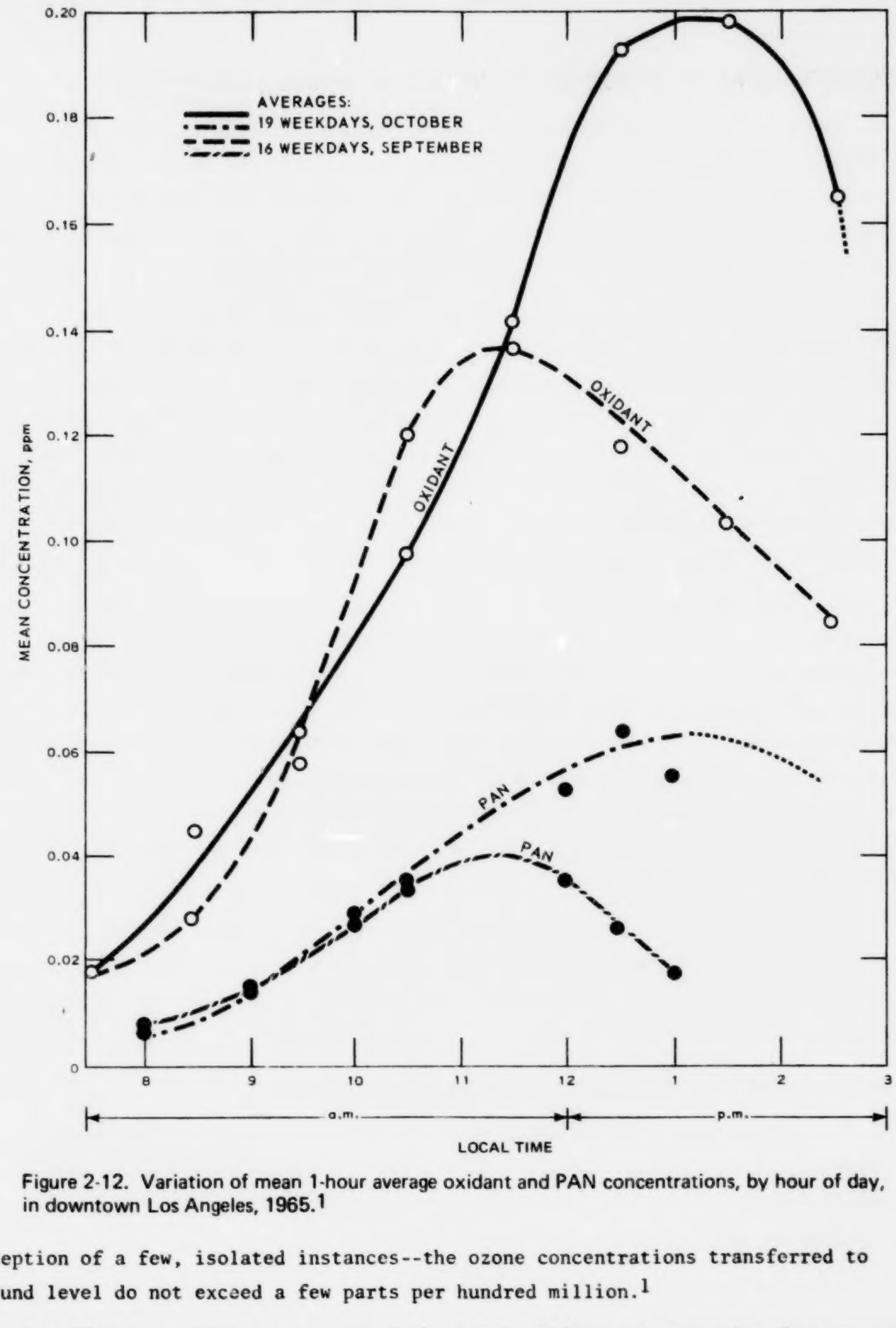

Figure 2-12. Variation of mean 1-hour average oxidant and PAN concentrations, by hour of day, in downtown Los Angeles, 1965.[1]

exception of a few, isolated instances--the ozone concentrations transferred to ground level do not exceed a few parts per hundred million.[1]

In efforts to obtain a measure of the total oxidant concentration from natural sources, measurements were made in several nonurban locations. Results from such early studies showed the oxidant in these areas to range mainly from less than 0.01

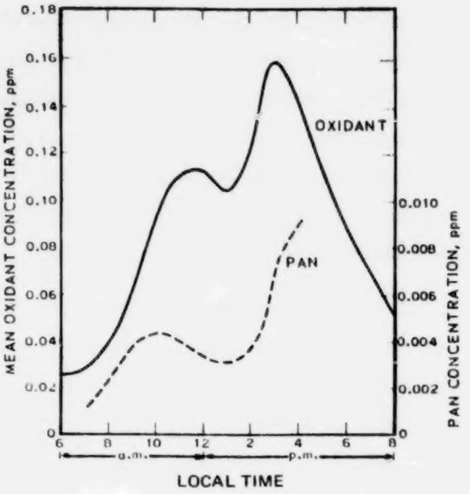

Figure 2-13. Variation of mean 1-hour average oxidant and PAN concentrations, by hour of day, at the University of California at Riverside, September 1966.[1]

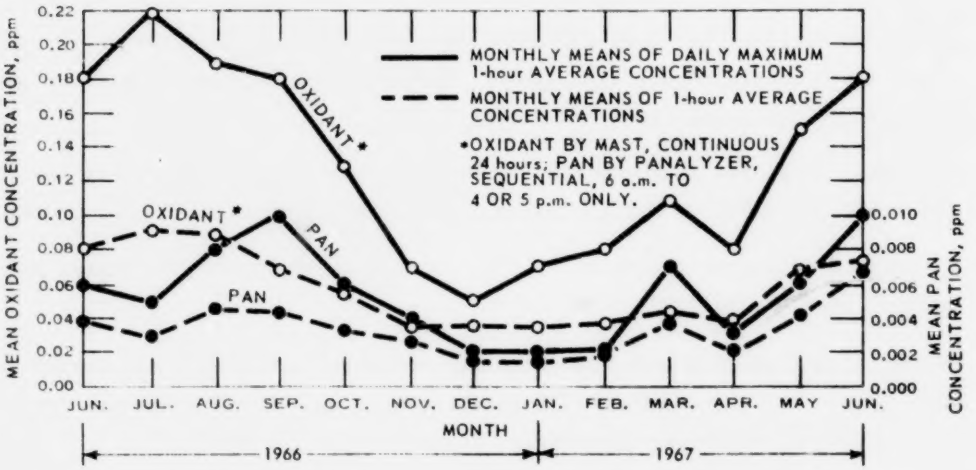

Figure 2-14. Monthly variation of oxidant and PAN concentrations at the University of California at Riverside, June 1966- June 1967.[1]

to 0.04 ppm, with occasional readings as high as 0.07 ppm.[1] More recent studies, however, revealed frequent occurrence of oxidant concentrations exceeding the air quality standard (0.08 ppm O_3) in several rural areas in the continental United States.[7,8] These studies provided strong indications that a part of the oxidant found in nonurban areas may result from transport of pollutants from urban areas.

Some clarifications must be made here in regard to the significance of these concentrations of naturally formed oxidant. First, such concentrations are not negligible; they may amount to as much as 50 percent or more of the level taken in the United States to be the air quality standard for ozone (0.08 ppm O_3).[9] Second, although these concentrations occur in the absence of anthropogenic emissions, this does not necessarily mean that in the presence of anthropogenic sources the observed oxidant is simply the sum of the natural and the anthropogenic contributions. The chemistry of oxidant formation from hydrocarbons and nitrogen oxides suggests that the combination of natural and man-made emissions (hydrocarbons and nitrogen oxides) can result in oxidant concentrations that can be either larger or smaller than the sum of the concentrations caused by the two emission sources individually.

In conclusion then, the oxidant concentrations from natural sources, although not unequivocally established, almost certainly are not negligible. Further, assessment of the importance of these sources is not simple. The levels of oxidants observed in areas free of human activities are not necessarily indicative of the contribution of the natural sources to the oxidant observed in urban atmospheres.

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CHAPTER 3. CHEMISTRY OF OXIDANT FORMATION

INTRODUCTION

When photochemical oxidants in air were identified as products of a photochemical process involving primary air pollutants, it became apparent immediately that the problem could not be abated by traditional methods of direct control. The chemistry of this process had to be clearly understood before rational abatement measures could be devised. Accordingly, in the ensuing years, numerous studies of the oxidant chemistry were conducted with the following specific objectives:

1. To identify the precursors of photochemical oxidants, that is, those primary pollutants that participate as reactants in the oxidant-forming process.
2. To determine the kinetics of the precursor reactions mainly for the purpose of deducing the impact of precursor control upon oxidant formation.
3. To determine the stoichiometry of the precursor reactions for the purpose of more fully assessing the pollution problems caused by such precursors.
4. To elucidate in detail the oxidant-forming mechanism for the purpose of providing theoretical--as distinct from empirical--input to the oxidant abatement effort, and also for the purpsoe of relating oxidant formation to other manifestations of photochemical pollution.

Several of these objectives have been achieved--at least to a degree of completion such that the information generated was sufficiently comprehensive and reliable to permit development of a crude but promising oxidant abatement strategy. Because of their importance in the case made here regarding the photochemical oxidant problem, these studies of the oxidant chemistry are presented and briefly discussed in this report. The discussion is focused on those findings that are most noteworthy and most relevant to a delineation of the photochemical oxidant problem.

MECHANISM OF OXIDANT FORMATION

The pioneering work of Haagen-Smit and his collaborators in 1952[1] first demonstrated through laboratory experimentation that the photochemical oxidants present in an urban atmosphere may indeed be products of atmospheric photochemical reactions involving organic and inorganic (nitrogen oxides) pollutants. Since then numerous studies of the oxidant formation phenomenon have been conducted,[2-5] and a wealth of information regarding the stoichiometry, kinetics, and mechamisms of these hydrocarbon

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(HC)-nitrogen oxide (NO_x)-air-sunlight reactions in now available. The following discussion summarizes the results of these studies and presents the chemical mechanism that is presently thought to best explain the phenomenon of photochemical oxidant formation.

All experimental research concerned with the mechanism of atmospheric oxidant formation was conducted in the laboratory using experimental conditions that were similar to, but not nearly as complex as, those prevailing in the real atmosphere. Such simplifications of the natural systems had to be made in order to facilitate research, but they also incurred penalty in terms of limitations on the validity of the research findings. Thus, most mechanistic evidence obtained to date pertains solely to the oxidant formation process occurring in the laboratory systems. The extent to which this laboratory evidence is applicable to the real atmosphere is not known with confidence and cannot be easily ascertained. The most that can be said at this time is that all of the reaction steps known to occur in the experimental reaction systems almost certainly occur in the real atmosphere also. The converse, however, is not necessarily true; that is, unidentified reaction steps may occur in the real atmosphere but not in the laboratory simulations.

The chemical changes that are observed to occur when a mixture of HC and NO_x pollutants is exposed to sunlight under conditions similar to those in atmosphere are illustrated in Figure 3-1. The diagrams of Figure 3-1 depict the overall photochemical process to consist of two distinct reaction stages occurring consecutively. During the first stage, nitric oxide (NO) is converted into nitrogen dioxide (NO_2) without any appreciable buildup of ozone (O_3) or other non-NO_2 oxidants. The second

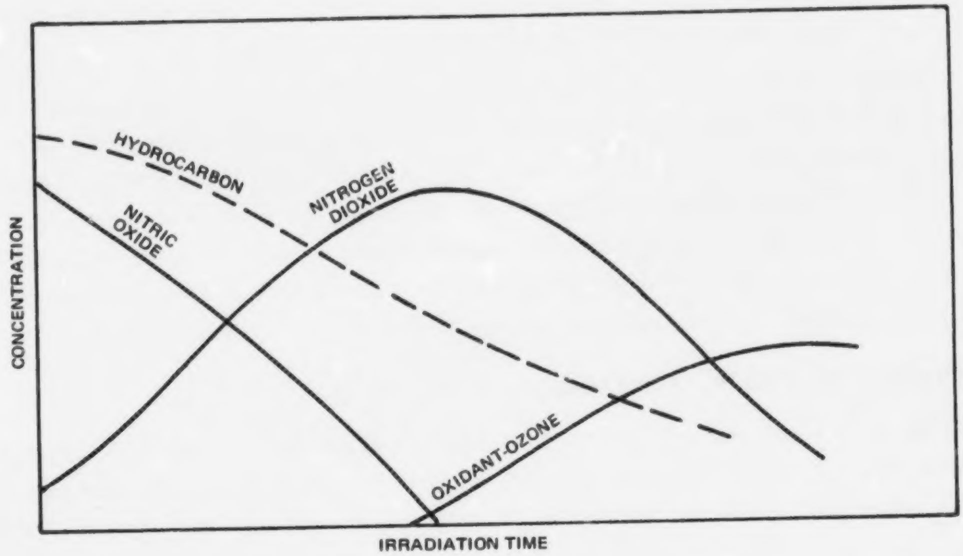

Figure 3-1. Chemical changes occurring during photoirradiation of hydrocarbon-nitrogen oxide-air systems.

stage starts when almost all the NO has been converted into NO_2 and is characterized by rapid accumulation of O_3 and other oxidant and nonoxidant type products. In the absence of HC reactant, the overall process maintains the two-stage profile except that the NO conversion process is now much slower, and the resultant O_3 concentrations--given adequate irradiation--are much smaller.

Kinetic mechanism explaining the observations depicted in Figure 3-1 have been postulated only in the last 10 years. The proposed mechanisms can be classified as either "specific" (written for the photooxidation of a specific hydrocarbon) or "lumped" (written for one or more species involving lumped reactants). The specific mechanisms, such as the one shown in Figure 3-2 for propylene[6] are as a rule more complex and provide a more detailed and hence more informative picture. Because of their complexity, however, specific mechanisms are nearly impossible to use in practical applications, such as in developing mathematical models that predict levels of oxidant in urban atmospheres based on levels of precursors. The difficulty arises mainly from the extreme multiplicity of reaction steps needed to describe the reactions of each of the numerous HC reactants present in urban air. This drawback in the specific mechanisms prompted the development of lumped mechanisms--mechanisms that are less descriptive of the fundamental chemistry involved but more useful in practical applications. An example of a lumped mechanism and its associated rate constant data is given in Figure 3-3 and Table 3-1, respectively.[7]

By either of the mechanisms given in Figures 3-2 and 3-3, ozone formation in the atmosphere appears to be the net result of the following main reactions:

$$NO_2 \xrightarrow[\text{light}]{\text{UV}} NO + O \qquad (3\text{-}1)$$

$$O + O_2 \xrightarrow{m} O_3 \qquad (3\text{-}2)$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad (3\text{-}3)$$

$$RO_x + NO \longrightarrow NO_2 + RO_y \qquad (3\text{-}4)$$

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (3\text{-}5)$$

(Where: RO_x and RO_y are organic and/or inorganic radicals that form only when organic reactants are present in the system.) Through this mechanistic procedure, the NO product from the photolysis of NO_2 reacts rapidly with and consumes O_3 to regenerate the photolyzed NO_2. Therefore, unless other processes convert the NO into NO_2, O_3 is not allowed to accumulate to important levels. However, other NO conversion processes do exist--mainly, the reactions of NO with RO_x and, to a much lesser degree, with molecular oxygen (O_2). The reaction with RO_x occurs only when photochemically reactive organic reactants are present, and is sufficiently rapid to cause atmospheric accumulation of O_3 to as much as 1 part per million (ppm) or more. In the absence of reactive organics, the only NO conversion process parallel to the O_3-NO reaction is

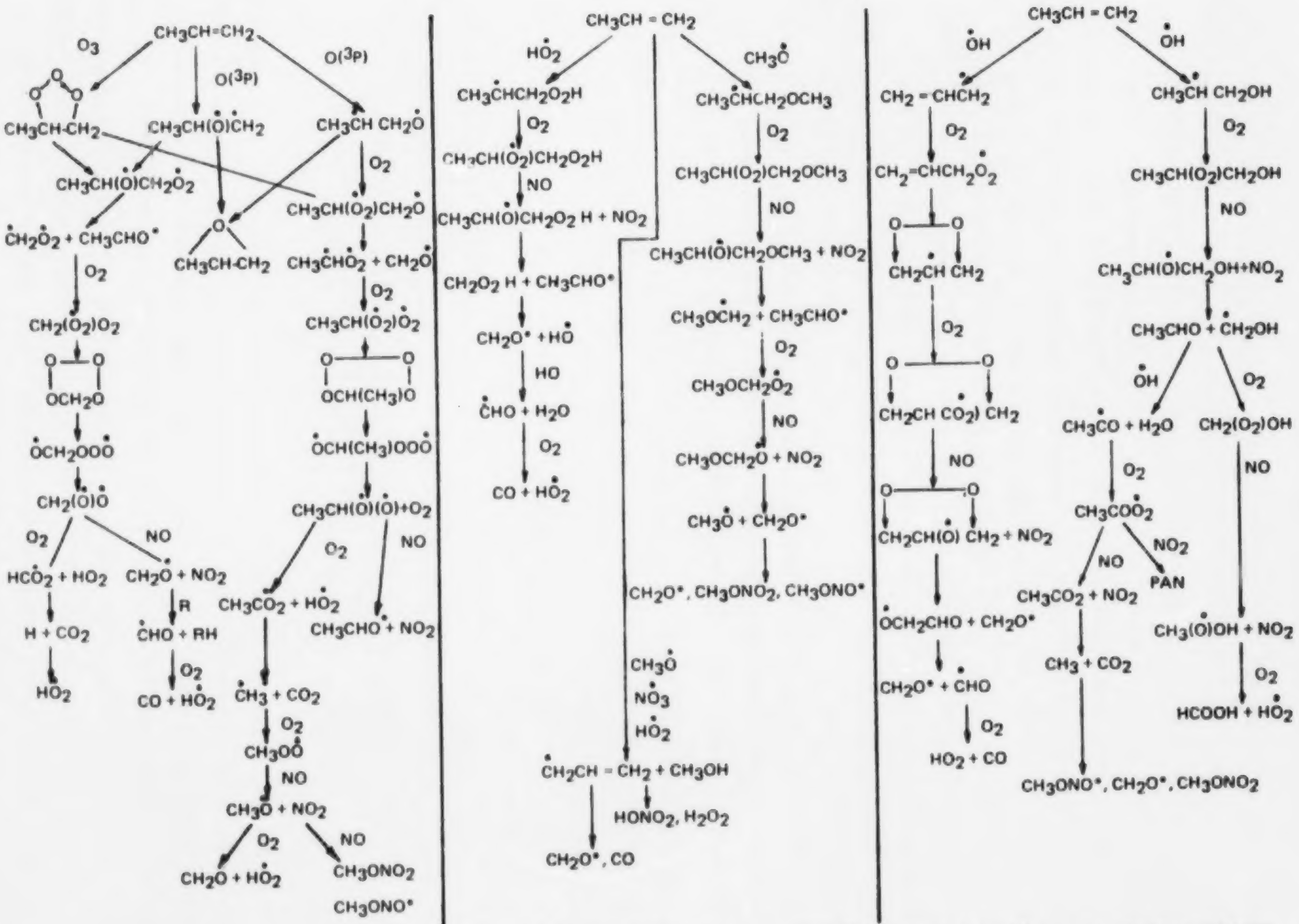

Figure 3-2. Flow diagram for propylene-nitrogen oxide-ultraviolet reaction system.[6] (Asterisk identifies products that undergo significant photodecomposition in sunlight.)

1. $NO_2 + h\upsilon \rightarrow NO + O$
2. $O + O_2 + M \rightarrow O_3 + M$
3. $O_3 + NO \rightarrow NO_2 + O_2$

The NO_2-NO-O_3 cycle

4. $O + NO + M \rightarrow NO_2 + M$
5. $O + NO_2 \rightarrow NO + O_2$
6. $O + NO_2 + M \rightarrow NO_3 + M$

Important reactions of O with inorganic species

7. $O_3 + NO_2 \rightarrow NO_3 + O_2$
8. $NO_3 + NO \rightarrow 2NO_2$
9. $NO_3 + NO_2 \rightarrow N_2O_5$
10. $N_2O_5 \rightarrow NO_2 + NO_3$
11. $N_2O_5 + H_2O \rightarrow 2HNO_3$

The chemistry of NO_3, N_2O_5, and HNO_3

12. $NO + HNO_3 \rightarrow HNO_2 + NO_2$
13. $HNO_2 + HNO_3 \rightarrow H_2O + 2NO_2$

Reactions of HNO_3 with inorganic species

14. $NO + NO_2 + H_2O \rightarrow 2HNO_2$
15. $2HNO_2 \rightarrow NO + NO_2 + H_2O$
16. $HNO_2 + h\upsilon \rightarrow OH + NO$

Chemistry of HNO_2

17. $OH + NO_2 \rightarrow HNO_3$
18. $OH + NO + M \rightarrow HNO_2 + M$
19. $OH + CO + (O_2) \rightarrow CO_2 + HO_2$

Important reactions of OH with inorganic species

20. $HO_2 + NO \rightarrow OH + NO_2$

Oxidation of NO by HO_2

21. $H_2O_2 + h\upsilon \rightarrow 2OH$

Photolysis of H_2O_2

22. $HC_1 + O \rightarrow ROO + \alpha R\underset{\overset{\|}{O}}{C}OO + (1\text{-}\alpha)\ HO_2$
23. $HC_1 + O_3 \rightarrow R\underset{\overset{\|}{O}}{C}OO + RO + HC_4$
24. $HC_1 + OH \rightarrow ROO + HC_4$
25. $HC_2 + O \rightarrow ROO + OH$
26. $HC_2 + OH \rightarrow ROO + H_2O$
27. $HC_3 + O \rightarrow ROO + OH$
28. $HC_3 + OH \rightarrow ROO + H_2O$
29. $HC_4 + h\upsilon \rightarrow \beta ROO + (2\text{-}\beta)\ HO_2$
30. $HC_4 + OH \rightarrow \beta R\underset{\overset{\|}{O}}{C}OO + (1\text{-}\beta)HO_2 + H_2O$

Organic oxidation reactions

HC_1 = Olefins
HC_2 = Aromatics
HC_3 = Paraffins
HC_4 = Aldehydes

31. $ROO + NO \rightarrow RO + NO_2$
32. $R\underset{\overset{\|}{O}}{C}OO + NO + (O_2) \rightarrow ROO + NO_2 + CO_2$
33. $R\underset{\overset{\|}{O}}{C}OO + NO_2 \rightarrow R\underset{\overset{\|}{O}}{C}OONO_2$
34. $RO + O_2 \rightarrow HO_2 + HC_4$
35. $RO + NO_2 \rightarrow RONO_2$
36. $RO + NO \rightarrow RONO$

Reactions of organic free radicals with NO, NO_2, and O_2

37. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
38. $HO_2 + ROO \rightarrow RO + OH + O_2$
39. $2ROO \rightarrow 2RO + O_2$

Other peroxy radical reactions

Figure 3-3. A lumped kinetic mechanism for photochemical smog.

Table 3-1. VALIDATION VALUES OF RATE CONSTANTS AND THEIR COMPARISON WITH THE RECOMMENDED VALUES OF INVESTIGATIONS[a]
($ppm^{-1}min^{-1}$ unless indicated otherwise)

Reaction (Figure 3-3)	Validation value	Demerjian et al. (1973)	Johnston et al. (1970)	Niki et al. (1972)	Others
1	$0.266\ min^{-1}$				
2	$2.0 \times 10^{-5} ppm^{-2} min^{-1}$	2.0×10^{-5}	2.3×10^{-5}	2.2×10^{-5}	
3	20.8	2.3×10^{1}	2.9×10^{1}	2.9×10^{1}	20.8[d]
4	$3.5 \times 10^{-3} ppm^{-2} min^{-1}$	3.4×10^{-3}	2.5×10^{-3}		
5	1.38×10^{4}	8.1×10^{3}	8.1×10^{3}		1.38×10^{4} e
6	$2.2 \times 10^{-3} ppm^{-2} min^{-1}$	2.2×10^{-3}			
7	4.6×10^{-2}	$0.48\text{-}1.1 \times 10^{-1}$	1.1×10^{-1}	1.1×10^{-1}	4.6×10^{-2} d
8	1.5×10^{4}	$0.66\text{-}1.47 \times 10^{4}$	1.5×10^{4}	1.5×10^{4}	
9	4.5×10^{3}	6.8×10^{3}	4.5×10^{3}	4.4×10^{3}	
10	$1.5 \times 10^{1} min^{-1}$	1.5×10^{1}	1.4×10^{1}	1.4×10^{1}	
11	1.0×10^{-5}	2.5×10^{-3}	3.0×10^{-3}	1.5×10^{-6}	$\leq 2 \times 10^{-5}$ f
12	2.5×10^{-4}				2.5×10^{-4} g
13	0.2				≤ 0.2[h]
14	$2.1 \times 10^{-6} ppm^{-2} min^{-1}$	$\leq 4.3 \times 10^{-6}$	6.9×10^{-6}	3.6×10^{-8}	
15	4.5	≤ 4.5		2.8×10^{-2}	
16	$1.3 \times 10^{-2} min^{-1}$	$1/4 \times k_1$	$1/10 \times k_1$	$1/2000 \times k_1$	
17	1.5×10^{4}	$\geq 1.5 \times 10^{4}$	1.5×10^{3}	6.0×10^{3}	
18	1.2×10^{4} b	$0.8 \times k_{17}$		2.1×10^{3}	
19	2.5×10^{2}	2.5×10^{2}	2.2×10^{2}	2.6×10^{2}	
20	7.0×10^{2}	2.0×10^{2}		2.9×10^{2}	7.0×10^{2} i
21	$1/250\ k_1 min^{-1}$	$1/160\ k_1$			$1/250 \times k_1$ j
22	6.8×10^{3}	6.8×10^{3}	$3.7\text{-}4.4 \times 10^{3}$	4.4×10^{3}	
23	1.6×10^{-2}	1.5×10^{-2}	$0.9\text{-}1.6 \times 10^{-2}$	1.7×10^{-2}	

Table 3-1 (continued). VALIDATION VALUES OF RATE CONSTANTS AND THEIR COMPARISON WITH THE RECOMMENDED VALUES OF INVESTIGATIONS[a] ($ppm^{-1}min^{-1}$ unless indicated otherwise)

Reaction (Figure 3-3)	Validation value	Demerjian et al. (1973)	Johnston et al. (1970)	Niki et al. (1972)	Others
24	2.5×10^4	9.4×10^3		2.5×10^4	
25	1.07×10^2 [c]		1.07×10^2		
26	8×10^3 [i]				
27	6.5×10^1	3.2×10^1	$0.16\text{-}6.5 \times 10^1$		
28	3.8×10^3	6.4×10^3	5.7×10^3		6.0×10^3 [k], 3.8×10^3 [ℓ]
29	$2.5 \times 10^{-3} min^{-1}$	$0.4\text{-}2.5 \times 10^{-3}$		$1/1000 \times k_1$	
30	2.3×10^4	2.2×10^4	2.3×10^4		
31	9.1×10^2	9.1×10^2		2.9×10^2	
32	9.1×10^2	4.7×10^2		1.5×10^3	
33	1.0×10^2	4.9×10^2		2.2×10^1	
34	2.4×10^{-2}	$2.4\text{-}5.6 \times 10^{-2}$		4.4×10^{-3}	
35	4.9×10^2	$3.0\text{-}4.9 \times 10^2$		2.9×10^3	
36	2.5×10^2	$2.0\text{-}2.5 \times 10^2$		9.9×10^2	
37	5.3×10^3	5.3×10^3	5.3×10^3	5.3×10^3	
38	1.0×10^2	1.0×10^2		5.3×10^3	
39	1.0×10^2	1.0×10^2		4.4×10^3	

[a] Sources as cited by Demerjian.[7]

[b] Pseudo second-order value.

[c] These values are for toluene. Because the experimental data considered did not include aromatic hydrocarbons, these two values were not used in the validation exercises.

[d] Ghormley et al. (1973).

[e] Schuck et al. (1966).

[f] Morris and Niki (1973).

[g] Jaffe and Ford (1967).

[h] Based on thermodynamic considerations. This reaction probably proceeds heterogeneously, and the reverse reaction may be important, although it was not included here.

[i] Davis et al. (1972).

[j] Unpublished value measured in the Chemistry and Physics Laboratory of EPA.

[k] Morris and Niki (1971).

[ℓ] Demerjian et al. (1973) employed 6.4×10^3 $ppm^{-1}min^{-1}$ in their modeling studies because that value provided a better fit to the rate of removal of n-butane than the value of 3.8×10^3 $ppm^{-1}min^{-1}$ measured by Greiner (1970).

the reaction of NO with O_2; this reaction, however, is relatively slow and does not cause significant O_3 accumulation.

In mathematical terms, the O_3 buildup in the atmosphere is given by the equation:[6]

$$[O_3] = kI \frac{[NO_2]}{[NO]} \qquad (3\text{-}6)$$

derived by applying the steady state hypothesis to chemical reaction steps 3-1, 3-2, and 3-3. In Equation 3-6, I designates light (sunlight) intensity, and k is a constant. By this equation, any process that converts NO into NO_2--such as the reaction of NO with RO_x--tends to cause high $[NO_2]/[NO]$ ratios, and hence high levels of O_3 buildup.

The mechanistic picture described in the preceding paragraphs suggests at first glance that any organic reactant that is capable of causing rapid conversion of NO into NO_2 should also cause formation of high levels of O_3. This, however, is only partially true. In a generalized sense, O_3 yield depends not only on the ability of the organic reactant to oxidize the NO, but also on the tendency of the organic reactant to react with and destroy O_3 and on the nature and mechanistic role of the products that result from the photooxidative degradation of the organic reactant.

Presently, the mechanism shown in Figure 3-2, although highly speculative because it has not been validated yet over a wide range of reactant concentrations, is believed to be reasonably valid and complete. However, it should be stressed that this mechanism is limited in that it applies only to laboratory systems--more specifically, to propylene-NO_x-air mixtures that are photoirradiated in a smog chamber. As mentioned previously, the mechanism of the oxidant-forming process in a real atmosphere containing a multitude of reacting pollutants may include reaction steps in addition to those listed in Figure 3-2. Such additional reactions known or suspected to occur in the real atmosphere may include, for example, photolysis of aldehydes, of ketones, and of lead halides and follow-up reactions of the products from such photolyses. Additional photochemical reactions may also be caused through energy transfer processes promoted by pollutants capable of absorbing solar energy and of transferring such energy to nonabsorbing pollutants. Finally, additional reactions of importance may occur on the surface of the aerosol particles suspended in air. The question regarding the roles, if any, of all these reactions in the oxidant-forming process that occurs in the real atmosphere is an open one. Additional research must be done before answers are obtained.

HYDROCARBON REACTIVITY

From an air pollution standpoint, the photochemical reactivity--or "reactivity"--of an organic pollutant denotes the intrinsic ability of the pollutant to participate in atmospheric chemical reactions that result in photochemical smog formation. The concept of hydrocarbon reactivity (the term "hydrocarbon" is meant here to encompass all organic substances) was developed when laboratory research showed that different organic substances, when exposed to atmospheric conditions, do not react similarly. Specifically, when traces of an individual organic and NO in air were irradiated with artificial sunlight, the resultant levels of smog--in terms of eye irritation, plant damage, visibility reduction, and material damage--were found to vary widely with the chemical structure of the organic reactant. The same laboratory studies also revealed that these smog manifestations, as a rule, were accompanied by manifestations of chemical activity, such as disappearance of the organic reactant, rapid conversion of NO into NO_2, and formation of products. As a result of these studies, the concept of hydrocarbon reactivity has evolved to include several reactivity types, each type corresponding to a specific chemical or biological manifestation of photochemical smog. Hydrocarbon reactivity has been defined and expressed in terms of the following·[8]

1. Rate of disappearance of organic reactant from irradiated organic-NO-air mixtures.
2. Rate of conversion of NO into NO_2.
3. Yield of ozone or oxidant.
4. Yield of aldehydes and peroxyacyl nitrates.
5. Formation of aerosols.
6. Damage to plants.
7. Irritation of eyes.

The fact that organic substances differ greatly in reactivity is extremely significant from a pollution control standpoint because it introduces the option of selective control of organic emissions as an alternative to indiscriminate control. In principle at least, this reactivity-based control is believed to be the superior approach, and it is for this reason that considerable research effort has been expended in obtaining reactivity data for organics and in exploring application of such data in the development of control strategies. Such reactivity data presently available, methods for obtaining them, and their application in control practices are discussed next.

Because of the early recognition of hydrocarbon pollutants, a relative abundance of reactivity data for HC is available. Data for nonhydrocarbon organics cover a large variety of organic compounds but are not as comprehensive and reliable as those for HC. Information, obtained through 1965, on several types of HC reactivity was compiled and anlyzed by Altshuller[9] and presented in terms of a reactivity classification of hydrocarbons, as shown in Table 3-2. The Altshuller analysis is an attempt to derive a single reactivity rating for each hydrocarbon that presumably represents the composite of all reactivity types mainifested by that hydrocarbon. This reactivity rating, which will be discussed later, has only limited validity,

Table 3-2. COMPARISON OF REACTIVITIES OF DIFFERENT TYPES OF ORGANICS[9]

Substance or subclass	Reactivity on 0 to 10 scale						
	Ozone or oxidant	Peroxy-acyl nitrate	Formal-dehyde	Aerosol	Eye irrita-tion	Plant damage	Overall reactivity
C_1-C_3 paraffins	0	0	0	0	0	0	0
Acetylene	0	0	0	0	0	0	0
Benzene	0	0	0	0	0	0	0
C_4+ -paraffins[a]	0-4	0[d]	0[d]	0	0[d]	0	1
Toluene (and other monoalkylbenzenes)	4	ND[e]	2	2	4	0-3	3
Ethylene	6	0	6	1-2	5	+[d]	4
1-alkenes[b]	6-10	4-6	7-10	4-8	4-8	6-8	7
Diolefins	6-8	0-2	8-10	10	10	0[d]	6
Dialkyl- and trialkyl-benzenes	6-10	5-10	2-4	+[f]	4-8	5-10	6
Internally double-bonded olefins	5-10	8-10	4-6	6-10	4-8	10	8
Aliphatic aldehydes	5-10	+[f]	+[f]	ND[e]	+[f]	+[d,f]	--

[a] Averaged over straight-chain and branched-chain paraffins.

[b] Includes measurements on propylene through 1-hexene, 3-ethyl-1-butene and 2,4,4-trymethyl-1-1-pentene.

[c] Includes measurements on straight-chain butenes through heptanes with double-bond in 2 and 3 position, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclohexene.

[d] Very small yields or effects may occur after long irradiations.

[e] No experimental data available.

[f] Effect noted experimentally, but data insufficient to quantitate.

but it does provide a first-approximation measure of a hydrocarbon's ability to cause photochemical smog.

Since 1965, other investigators have reported reactivity studies, including detailed reactivity data on hydrocarbon and nonhydrocarbon organics:

Investigator	Description of Study
Heuss and Glasson[10] (General Motors)	Eye initiation, rate of NO_2 formation, and product yield reactivity data for hydrocarbons.
McReynolds et al.[11]	Reactivity data for hydrocarbon disappearance.
Sturm et al.[12]	Rate of NO_2 formation and product yield reactivity data for hydrocarbons.
Dimitriades and Wesson[13] (Bureau of Mines)	Rate of NO_2 formation and product yield reactivity data for aldehydes.
Levy and Miller[14] (Battelle)	Reactivity data for solvent organics.
Wilson and Doyle[15] (Stanford Research Institute)	Reactivity date for solvent organics.
Laity et al.[16] (Shell)	Reactivity data for solvent organics.
Miller et al.[17]	Aerosol reactivity data for hydrocarbons.
Brunell et al.[18] (LAAPCD)	Reactivity data for solvent organics.

Reactivity data reported to date for hydrocarbon and nonhydrocarbon organics are too numerous to be included here in their totality. Instead, this report will be limited to presenting only those reactivity data that pertain to the oxidant-forming potential or organics. The presentation will also include a description of the reactivity measurement procedures as well as a brief discussion of the quality and utility of the existing oxidant-reactivity data.

The procedure commonly used for reactivity measurement is to irradiate clean air mixed with the organic reactant vapor, NO, and NO_2 at prescribed concentrations (parts per million) in a smog chamber and to measure the disappearance of reactants, the formation of products, and the intensity of biological effects. When the aerosol-forming potential of the organic is of interest, sulfur dioxide, at a prescribed concentration, is also included in the reactant mixture. Experimental conditions for such measurement are, to the extent feasible and practical, similar to the conditions typically present in an urban atmosphere. Thus, the reactant concentrations, the intensity and spectral characteristics of radiation, the irradiation time and temperature, and often the relative humidity are comparable to actual conditions, such as those in the Los Angeles air basin during a sunny summer day.

The oxidant reactivity studies referred to in the following paragraphs can be described briefly as follows:

1. The General Motors (GM) study[10] of hydrocarbon reactivity used a 300-cubic-foot (ft^3) stainless steel and glass smog chamber. Initial reactant concentrations in the chamber were 2 ppm for hydrocarbon and 1 ppm for NO_x.

2. The Bureau of Mines (BOM) studies on hydrocarbon reactivity and on aldehyde reactivity[13] used a 100-ft^3 aluminum and glass chamber with initial reactants at 1.0 ppm for hydrocarbon (or aldehyde) and 0.5 ppm for the NO_x.

3. The Los Angeles County Air Pollution Control District (LAAPCD) study[18] of solvent reactivity used a 1200-ft^3 glass and aluminum chamber. Initial concentrations of reactants in the chamber ranged widely; for the data reported here, the solvent vapor concentration ranged from 5.0 to 7.8 ppm; the NO_x from 1.7 to 2.1 ppm.

4. The Battelle study[14] of solvent reactivity used a 600-ft^3 aluminum and Teflon chamber. Initial solvent vapor and NO_x concentrations were 4.0 ppm and 2.0 ppm, respectively.

5. The Stanford Research Institute (SRI) study[15] of solvent reactivity used a 268-ft^3 aluminum and glass chamber with internal surfaces coated with Teflon. Solvent vapors were tested either individually or in combination with a standard HC mixture. In the individual-solvent tests, initial solvent vapor and NO_x concentrations were 1 ppm and 0.10 to 0.28 ppm, respectively. In the solvent-HC mixture tests, initial solvent vapor concentration was 4 ppm or 8 ppm; initial NO was 0.03 to 0.25 ppm; initial NO_2 was 0.40 to 1.10 ppm.

6. The Shell study[16] of solvent reactivity used mainly a 397-liter stainless steel chamber and to a lesser extent a 235-liter and a 23-liter glass chamber. Initial solvent vapor and NO_x concentrations were 1.5 ppm and 0.6 ppm, respectively.

7. A considerable amount of reactivity data were also obtained from earlier studies reviewed by Altshuller and Bufalini.[4]

The oxidant-reactivity data obtained in all these studies consisted of data on the maximum oxidant concentration observed during the irradiation test and on the oxidant dosage, that is, the time-integrated concentration of oxidant. Such reactivity data, however, are not satisfactory, mainly because they are extremely sensitive to variations in smog chamber design and measurement conditions. The problem is somewhat reduced by expressing reactivities of organics as measured in one smog chamber in relation to the reactivity of a reference organic as measured in the same chamber. A similar technique is the "reactivity scale" technique by which the reference organic is chosen to be the most reactive organic known and is arbitrarily assigned a reactivity rating of 10 (or 100); thus, reactivities of organics are expressed in terms of ratings ranging from 0 to 10 (or 100). In the present case, the oxidant-reactivities of the organics tested in the aforementioned studies are expressed in terms of the maximum oxidant concentration relative to the maximum oxidant concentration for toluene. The principal reason for choosing toluene as the reference organic is that toluene is a common test-organic in most of the reactivity measurement programs reported. Such oxidant-reactivity data for various hydrocarbon and nonhydrocarbon organics are given in summary form in Tables 3-3 and 3-4.

Reactivity data, such as those in Tables 3-3 and 3-4, are useful in that they provide a degree of discrimination of the organic pollutants, based on the ability of such pollutants to produce photochemical oxidant. These data, however, have limitations. To illustrate the nature and magnitude of these limitations, it is necessary that the intended use of the reactivity data first be considered.

As mentioned previously, the reactivity data are intended to provide a guide in developing selective control strategies. Conceptually, such a strategy entails reduction of each individual organic emission component to a degree commensurate with the component's relative reactivity. In practice, selective control can be implemented either by development of different emission rate standards for the different organic emissions or by development of a reactivity standard for the emission mixture. Either application introduces demands in terms of consistency, interpretability, and abundance of reactivity data. Considering such applications and their demands, the existing oxidant-reactivity data are deficient in three respects.

First, the existing data are of limited internal consistency; that is, reactivity data obtained in different laboratories (for the same organics) are not in good agreement. The problem is probably caused by the diversity of smog chamber designs and reactivity measurement conditions used in the various laboratories. Expressing the reactivity of each organic in relation to the reactivity of a reference organic alleviates, but does not solve, the problem. The degree of agreement among data from different laboratories is illustrated in Figure 3-4, in which oxidant reactivities from the Battelle, Shell, and SRI studies are compared. Reasonable correlation is indicated for the Battelle-Shell data, but correlation of the Battelle-SRI data is poor.

Table 3-3. PHOTOCHEMICAL REACTIVITIES OF HYDROCARBONS

Hydrocarbon	Maximum oxidant-ozone, toluene equivalents[a]		
	BOM study[13]	GM study[10]	Other studies[4]
Methane	-	-	0
Ethane	-	-	0
Propane	-	-	0
n-butane	0.08	0.53	-
n-hexane	0.10	0.57	-
Iso-octane	0.13	0.63	-
n-nonane	-	-	0.4
Ethylene	1.55	0.93	1.9
Propylene	2.00	1.80	1.2
Butene-1	1.87	1.57	1.2
t-butene-2	1.99	1.47	-
cis-butene-2	2.08	1.47	-
2-me-butene-2	2.14	1.63	-
Hexene-1	1.70	1.37	1.2
Hexene-2	1.73	-	-
Tetra-me-ethylene	-	2.00	-
1,3-butadiene	2.51	1.60	2.0
Acetylene	-	-	0
Benzene	0	0.17	-
Toluene	1.00	1.00	1.0
Eth-benzene	0.92	0.70	-
n-prop-benzene	0	0.70	-
Iso-prop-benzene	0.79	0.63	-
n-but-benzene	-	0.80	-
Iso-but-benzene	-	0.57	-
sec-but-benzene	-	0.87	-
tert-but-benzene	-	0.43	-
o-xylene	1.49	1.07	-
m-xylene	-	1.30	1.3-2.0
p-xylene	1.37	0.87	-
*M*esitylene	1.73	1.53	2.3

[a] Toluene reactivity in terms of maximum oxidant-ozone concentration was: BOM: 0.355 ppm O_3; GM: 0.30 ppm O_3; other studies: 0.36 to 0.50 ppm O_3.

Second, the existing oxidant-reactivity data cannot be interpreted reliably in terms of relative contributions of the various organic pollutants to the photochemical oxidant observed in the real atmosphere. The problem here has two origins: (1) the exact conditions in the real atmosphere cannot be reproduced in smog chambers, (2) the existing reactivity data, which were obtained mostly from individual compound tests, are not necessarily adequate for predicting reactivities of organic pollutant mixtures such as those encountered in real atmospheres.

Third, the existing oxidant-reactivity data cover only those hydrocarbon and nonhydrocarbon organics that have been identified thus far in the atmosphere and in motor vehicle emissions. Many unidentified organic pollutants from diesel engines,

Table 3-4. REACTIVITIES AND CLASSIFICATION OF SOLVENTS

	Reactivity, toluene equivalents						
	Battelle[14]		SRI[15]		Shell[16]		
Solvent	Range	Avg.	Range	Avg.	Range	Avg.	Class
Paraffins (including cycloparaffins)	0.4-0.6	0.5	0.9-0.9	0.9	0.8-1.0	0.9	III
Olefins							
Aliphatic	1.3-1.5	1.4	-	-	1.8-3.1	2.4	V
Styrene	0.7	0.7	-	-	-	-	III
α-me-styrene	1.5	1.5	-	-	-	-	V
Aromatics							
Benzene	0	0	-	-	0.2	0.2	I
prim-,*sec*-alkyl benzenes	0.9-1.2	1.0	1.0	1.0	1.0-1.2	1.1	IV
tert-alkyl benzenes	0.6	0.6	-	-	0.5-0.5	0.5	II
Dialkyl-benzenes	1.0	1.0	-	-	1.3-1.7	1.5	IV
Tri-,tetraalkyl benzenes	1.5	1.5	-	-	3.2	3.2	V
Ketones							
Acetone	0	0	-	-	0.1	0.1	I
n-alkyl ketones	0.5-0.8	0.65	0.9	0.9	0.9-1.4	1.1	III
Branched alkyl ketones	1.0-1.8	1.4	0.9-1.0	0.95	1.3	1.3	IV
Cyclic ketones	0.2	0.2	0.5	0.5	0.5-0.6	0.5	II
Unsaturated ketones	1.5-1.7	1.6	-	-	-	-	V
Alcohols							
prim-,*sec*-alkyl alcohols	0.2	0.2	1.1-1.2	1.2	0.6-1.45	1.1	IV
tert-alkyl alcohols	-	-	-	-	0.3	0.3	I
Diacetone alcohol	1.4	1.4	1.7	1.7	-	-	V
Ethers							
Diethyl ether	-	-	-	-	2.5	2.5	V
Tetrahydrofuran	1.9	1.9	-	-	1.4	1.4	V
Ethyl cellosolves	1.5	1.5	1.9	1.9	-	-	V
Esters							
prim-,*sec*-alkyl acetates	0.2	0.2	0.7-1.4	1.0	0.8-1.0	0.9	III
tert-alkyl acetates	-	-	-	-	0.5	0.5	II
Cellosolve acetate	-	-	1.1	1.1	-	-	IV
Phenyl acetate	0	0	-	-	-	-	I
me-benzoate	0	0	-	-	-	-	I
Amines							
Ethyl amines	0.1-0.2	0.15	-	-	-	-	I
N-me-pyrrolidone	0.7	0.7	-	-	-	-	III
N,N-dime-formamide	-	-	-	-	0.2	0.2	I
N,N-dime-acetamine	-	-	-	-	0.95	0.95	III
Halocarbons							
Perhalogenated	-	-	0.5-0.5	0.5	-	-	II
Partially halogenated paraffins	-	-	0.8	0.8	-	-	III
Partially halogenated olefins	-	-	1.4	1.4	-	-	IV
Nitroalkanes							
2-nitropropane	0.2	0.2	0.7	0.7	-	-	II

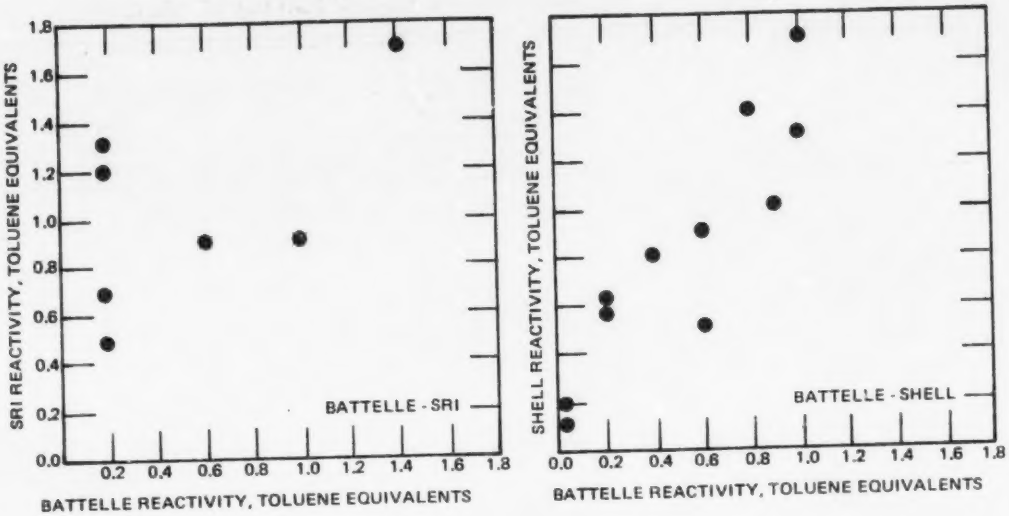

Figure 3-4. Correlation of solvent reactivity data from Battelle,[14] SRI,[15] and Shell[16] studies.

refineries, etc., undoubtedly exist in the atmosphere. Such pollutants need to be identified and their reactivities measured.

These imperfections of the presently available reactivity data, although real, do not necessarily altogether prohibit the use of reactivity criteria in control programs. Despite existing uncertainties, there is little doubt that organics such as methane, ethane, propane, acetylene, and benzene are not significant oxidant producers but that olefinic and polyalkyl benzene hydrocarbons are. Therefore, a limited use of the reactivity concept in control strategies for organic emissions is feasible.

As discussed in detail in Chapter 9, the present oxidant abatement strategy in the United States consists of the following regulations and recommendations:

1. The national air quality standards for photochemical oxidants and for nonmethane hydrocarbons (NMHC) promulgated by the Federal government.[19] Unlike the oxidant standard, the NMHC standard--a 6 to 9 a.m. average concentration of 0.24 ppm C that is not to be exceeded more than once per year--is not meant to be an air quality goal; rather, it is to serve as a guide in devising implementation plans to achieve the oxidant standard. Methane was exempted from this restriction upon hydrocarbons mainly because of its low oxidant-forming potential.
2. The motor vehicle emission standards for total hydrocarbons promulgated by the Federal government.[20] Unlike the previous regulations, no hydrocarbon was exempted from the standards for this source--an obvious inconsistency.
3. The control guidelines for organic solvent emissions recommended by the Federal government.[21] Under these guidelines, all organic solvents are

assumed to be reactive except C_1 to C_5 n-paraffins, saturated halogenated hydrocarbons, perchloroethylene, benzene, acetone, cyclohexanone, ethyl acetate, diethylamine, isobutylacetate, isopropyl alcohol, methyl benzoate, 2-nitropropane, phenyl acetate, and triethylamine.

4. Control regulations for organic solvent emissions promulgated by individual state governments. Some states adopted the Federal government recommendations for exempt solvents; others adopted California Rule 66, which assumes all solvents to be nonreactive except certain olefinic, aromatic, and ketone-type organics.[22]

As suggested by these regulations, reactivity criteria were used in the formulation of the present oxidant abatement strategy in the United States, but in a somewhat inconsistent manner. Thus, the definitions of reactive (or of nonreactive) organics used in California Rule 66 and in the Federal guidelines for State Implementation Plans are consistent neither with each other nor with the definitions used in the motor vehicle emission standards and the air quality standards. This inconsistent use of the reactivity concept in present control practices is largely a result of compromises made in the interest of rationality, responsiveness to specific needs, and practicability of control regulations. The Federal government is now taking a closer look at the significance of this inconsistency problem and some corrective action may be taken.[23]

RELATIONSHIPS BETWEEN OXIDANT AND OXIDANT PRECURSORS

This section examines the functional relationships observed between photochemical oxidant (OX) and two oxidant precursors, hydrocarbons (HC) and nitrogen oxides (NO_x). In the United States, these relationships have been used as the sole basis for determining emissions control requirements for oxidant abatement. Because of this use, and because of the enormous economic and social impact of such control, these OX-HC-NO_x relationships became an extremely controversial issue and were the subject of numerous studies.

Early attempts to determine OX dependence on HC and NO_x consisted of smog chamber experimentation in which synthetic or automotive exhaust mixtures of HC and NO_x were photoirradiated under simulated atmospheric conditions. Results from those studies could not be interpreted with confidence mainly because the smog chamber methodology at the time was relatively crude and untested. More recently, the effort to obtain improved data on the OX-HC-NO_x relationships was expanded to include application of three different research approaches: (1) the aerometric data analysis approach; (2) the smog chamber approach, using improved techniques; and (3) the photochemical modeling approach. Presently, aerometric data analysis and smog chamber tests are the only methods capable of yielding usable information on the

$OX-HC-NO_x$ relationships; the photochemical modeling method is still in the developmental stage.

Observational Model[24,25]

The basic assumption in the observational model is that early-morning HC and NO_x levels are indicators of the OX levels that will occur later in the day. Specifically, the 6 to 9 a.m. HC and NO_x levels are compared with the daily 1-hour maximum OX levels that normally occur between 10 a.m. and 2 p.m. Because formation and accumulation of OX is influenced also by sunlight intensity, wind speed, and other meteorological conditions, a specific ambient combination of HC and NO_x will not always result in a specific maximum OX level. Rather, it will result in a range of maximum OX levels extending from zero (in days with total overcast, strong winds causing rapid dispersion, etc.) to an upper limit (obtained during days of bright sunshine, air stagnation, etc.). The level of this upper limit, obviously, will depend only on the concentrations of the precursors. It is this upper limit that the observational approach attempts to define.

The success of the observational approach depends critically on the number of days for which pollutant measurements are available. Oxidant values for any given combination of HC and NO_x precursors can range from zero to the upper limit. Because the upper limit is attained on only about 1 percent of the days in a year, measurements for many days are needed in order to provide reasonable assurance that an upper-limit point has actually been observed. The small number of data points in the vicinity of the upper-limit line shown in Figure 3-5 for the relationship between total nonmethane hydrocarbons (NMHC) and the maximum daily OX observed in several cities illustrates this point. (In this figure and throughout the chapter, hydrocarbons are measured in parts per million carbon, ppm C.) Because they are limited in number, these upper limit points may not define the true upper-limit oxidant line; more extensive observations would undoubtedly include still higher OX concentrations. It seems reasonable to conclude, however, that the upper-limit curve in Figure 3-5 is the most valid relationship available for the time period prior to 1969.

Oxidant values below 140 $\mu g/m^3$ (0.07 ppm) are omitted in Figure 3-5 because several factors indicate these values may be subject to measurement errors; however, the errors have no bearing on the upper-limit values. Likewise, the HC values below 200 $\mu g/m^3$ (0.3 ppm) are not reported--even though they may have a bearing on the upper-limit OX level--because they are subject to even greater measurement error.[26]

The curve of Figure 3-5 can be used to predict the maximum 1-hour-average OX concentration from a measured 6 to 9 a.m. average HC concentration. Likewise, the minimal level of HC that will produce a given OX level can also be predicted. For OX and HC levels below 0.1 ppm and 0.3 ppm C, respectively, numerical predictions

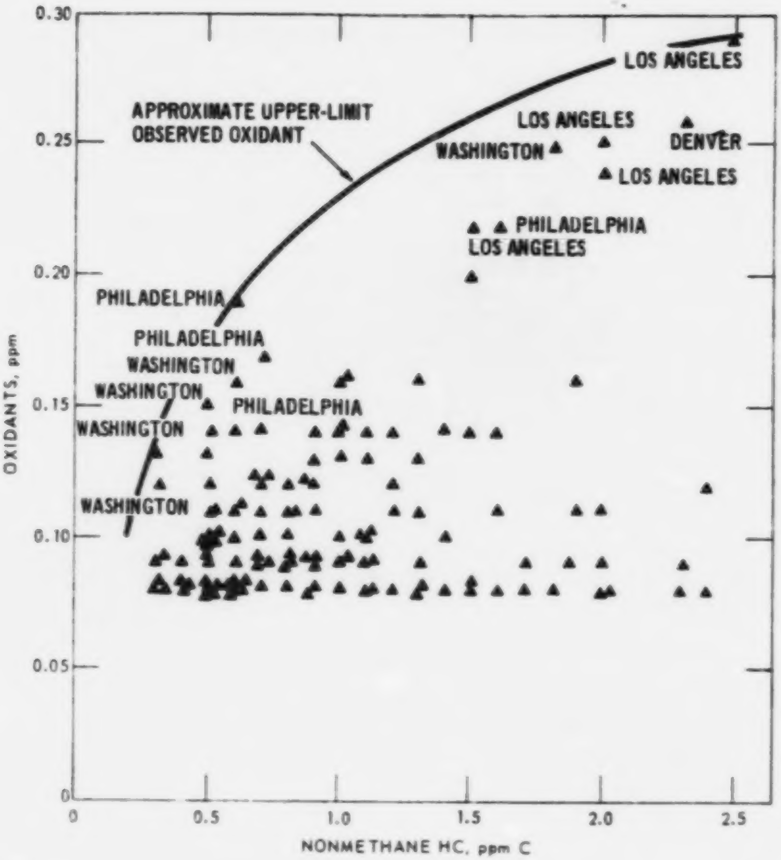

Figure 3-5. Maximum daily 1-hour-average oxidants as a function of 6 to 9 a.m. averages of nonmethane hydrocarbons at CAMP stations, June through September, 1966 through 1968, Los Angeles, May through October 1967.[24]

cannot be made. However, certain useful limitations can be defined; for example, it can be seen that for the OX to be below 0.1 ppm, NMHC must be below 0.3 ppm C.

An observational approach similar to the one used to derive the OX-HC relationship was used also in attempts to determine the dependence of OX on NO_x. In this case, the aerometric data analysis was guided by certain findings from smog chamber studies: (1) only NO and NO_2 are precursors of OX and (2) although the NO_2-to-NO ratio influences the rate of OX formation, it is the total NO_x concentration that determines the maximum OX concentration for given HC concentration and meteorological conditions. Plots of daily maximum OX versus average 6 to 9 a.m. NO_x concentrations for three cities are shown in Figures 3-6 through 3-8.[24] These plots show that OX levels below 0.1 ppm are associated with NO_x levels considerably below 0.1 ppm. This complicates the problem of determining the OX-NO_x relationship in the concentration range of interest because the NO_x data in this range suffer from considerable measurement error.

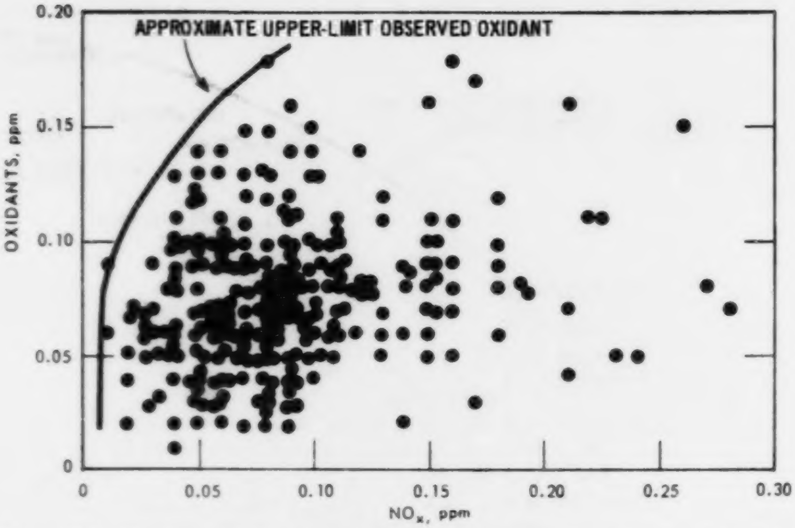

Figure 3-6. Maximum daily 1-hour-average oxidant concentrations as a function of 6 to 9 a.m. averages of total nitrogen oxides in Washington, D.C., June through September, 1966 through 1968.[24]

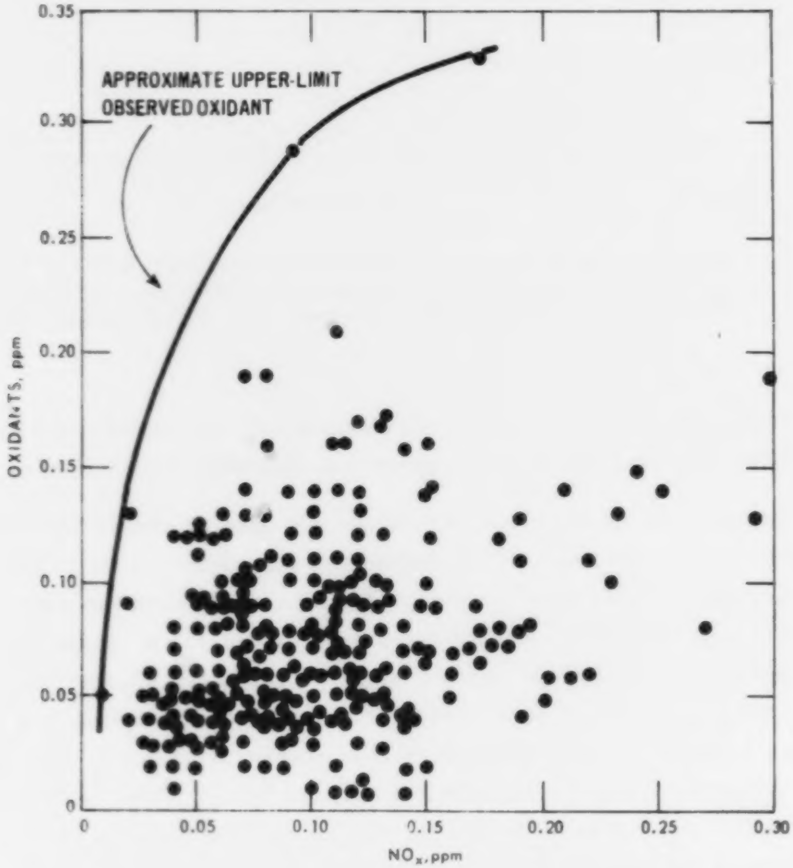

Figure 3-7. Maximum daily 1-hour-average oxidant concentrations as a function of 6 to 9 a.m. average total nitrogen oxides in Philadelphia, June through September, 1965 through 1968.[24]

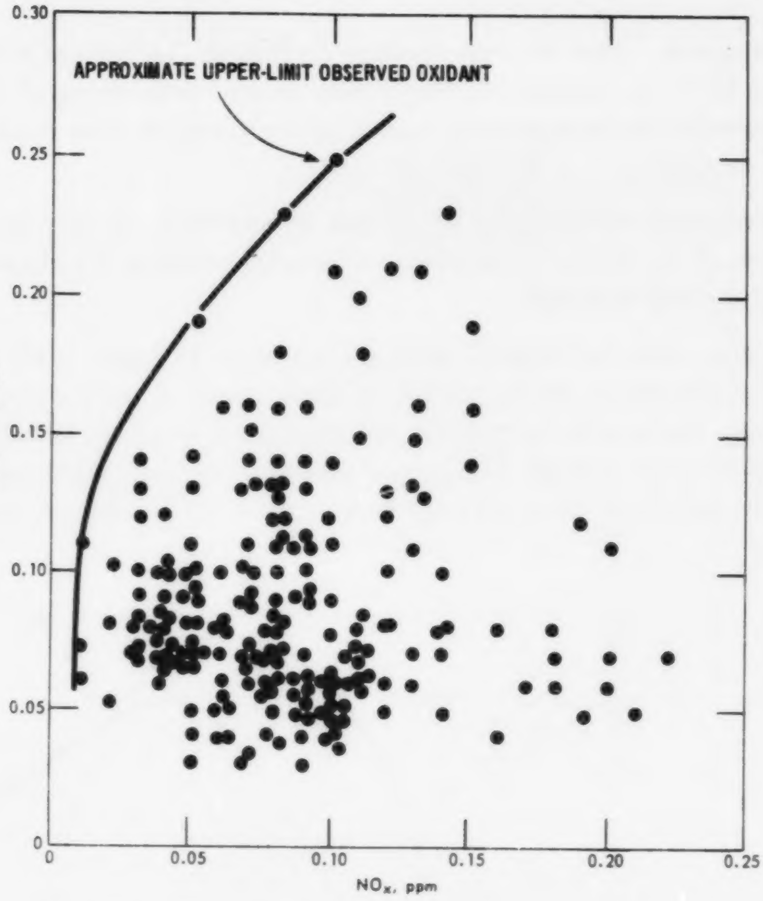

Figure 3-8. Maximum daily 1-hour-average oxidant concentrations as a function of 6 to 9 a.m. averages of total nitrogen oxides in Denver, June through September, 1965 through 1968.[24]

If all data points are accepted as equally valid, a reference value of 200 mg/m^3 (0.10 ppm) OX would be associated with as little as 20 mg/m^3 (0.01 ppm) NO_x. Because of the analytical uncertainties in the low concentration region, a more rational approach is to locate an NO_x level below which OX can be expected to exceed the reference concentration, that is, 200 mg/m^3 (0.10 ppm) OX, on 1 percent of the days. Figures 3-6 through 3-8 show only seven occasions when the OX equalled or exceeded 0.10 ppm and the NO_x was less than 0.04 ppm. This frequency represents about 1 percent of the combined data base.

Although the curves that define the maximum oxidant-forming potential in Figures 3-5 through 3-8 were drawn to include all the data points, they were not based on a statistical approach. The data were too limited in number to justify a statistical analysis; however, strict adherence to the limits set by the few applicable data points would associate an even lower value of NO_x with 200 mg/m^3 (0.10 ppm) OX. Current analytical uncertainties in the low-range measurements make such a conclusion unwise. From the relationships in Figures 3-6 through 3-8, it appears that the 6 to 9 a.m. average NO_x levels must be kept below 80 mg/m^3 (0.04 ppm) in order to prevent the maximum daily 1-hour OX concentration from reaching 200 mg/m^3 (0.1 ppm) or more.

The reference concentration of 0.1 ppm OX used here was selected on the basis of convenience; it is not the national air quality standard for oxidants (0.08 ppm) adopted in the United States.

Data from three Los Angeles locations are shown in Figure 3-9[26] for a calculated NMHC level of 1.5 ppm C. At two of these stations, a 6 to 9 a.m. value of 0.04 ppm NO_x, and a value of 0.05 ppm NO_x at a third site, are associated with a daily-maximum 1-hour-average OX concentration of 0.10 ppm. These Los Angeles results are similar to those obtained in Washington, D.C., Philadelphia, and Denver.

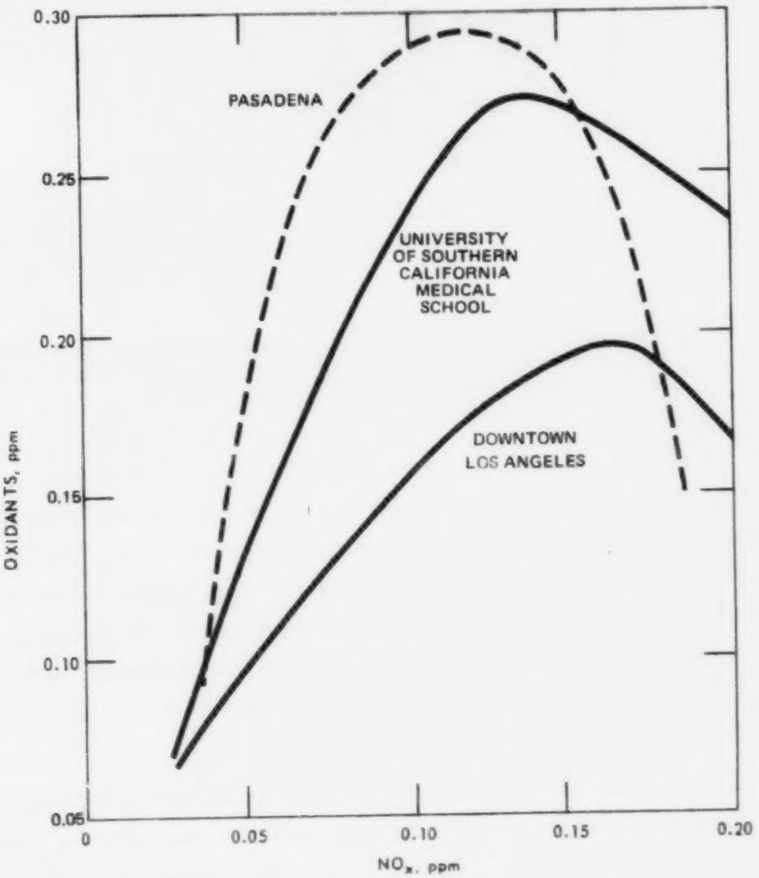

Figure 3-9. Upper limit of maximum daily 1-hour average oxidant concentrations, calculated nonmethane hydrocarbon concentration of 1.5 ppm C, as a function of average total nitrogen oxides from 6 to 9 a.m. at three Los Angeles stations, May through October 1967.[26]

For these reasons, the NO_x-OX relationship cited is considered the most reasonable that can be made at this time. It should be noted that the relationship states only that the 6 to 9 a.m. average NO_x must be below 80 µg/m^3 (0.04 ppm) to prevent oxidant levels greater than 200 µg/m^3 (0.1 ppm) from occurring more frequently than 1 percent of the time later in the day. It does not attempt to specify the exact NO_x concentration. Whether this or an even more stringent limitation of NO_x is required can be assessed only after further observations have been made of ambient atmospheres and the manner in which control of ambient HC concentration affects ambient OX levels. Laboratory results indicate that HC control, even in the absence of NO_x control, will definitely lead to reductions in ambient OX levels.

The preceding discussion dealt with the relationships of each individual precursor to maximum OX levels without considering combined effects. An initial attempt to explore the possible combined pollutant effects is shown in Figure 3-10

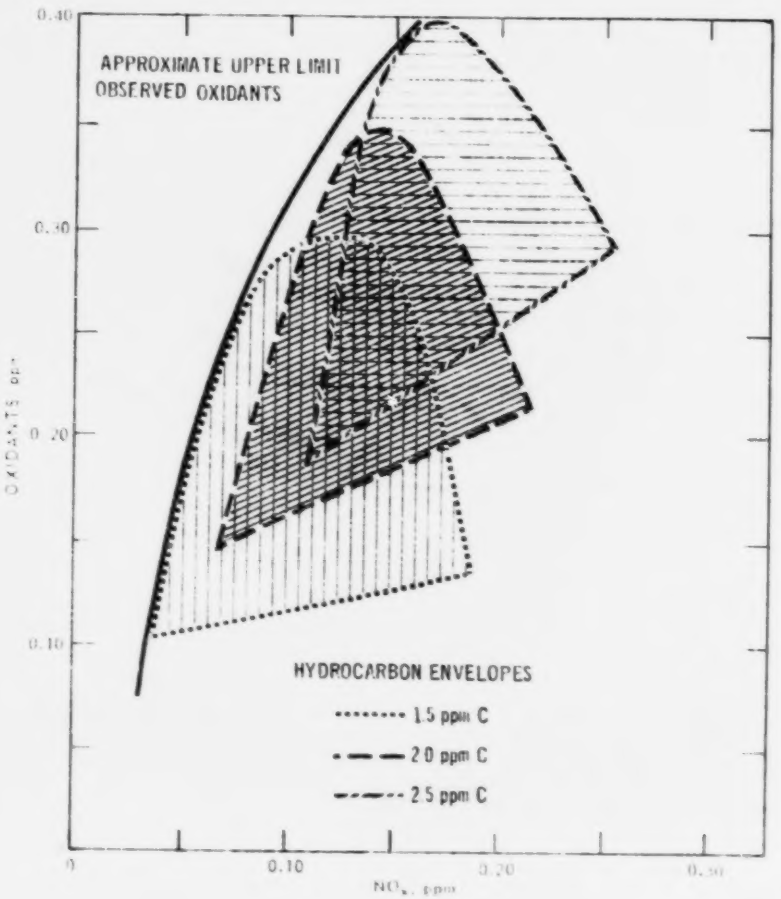

Figure 3-10. Nonmethane hydrocarbon-oxidant envelopes superimposed on maximum daily 1-hour average oxidant concentrations as a function of 6 to 9 a.m. average of total nitrogen oxides in Pasadena, California, May through October 1967.[24]

for Pasadena, California. In this figure, upper-limit OX-NMHC curves are superimposed on a graph to show the relationships of maximum OX levels to NO_x concentrations for different NMHC concentrations. These relationships cannot be very accurate, however, because of limitations in amount and comparability of data. For example, the NMHC data used were not measured directly; rather, they were calculated from total HC data, using established total HC-NMHC relationships.

Using the data available from CAMP stations, where NMHC is measured directly, the OX-NMHC-NO_x relationships appear to be as shown in Figure 3-11. Such relationships again show qualitative agreement with laboratory simultations (Figure 3-12),[27] but they are of questionable accuracy because they are based on insufficient ambient data.

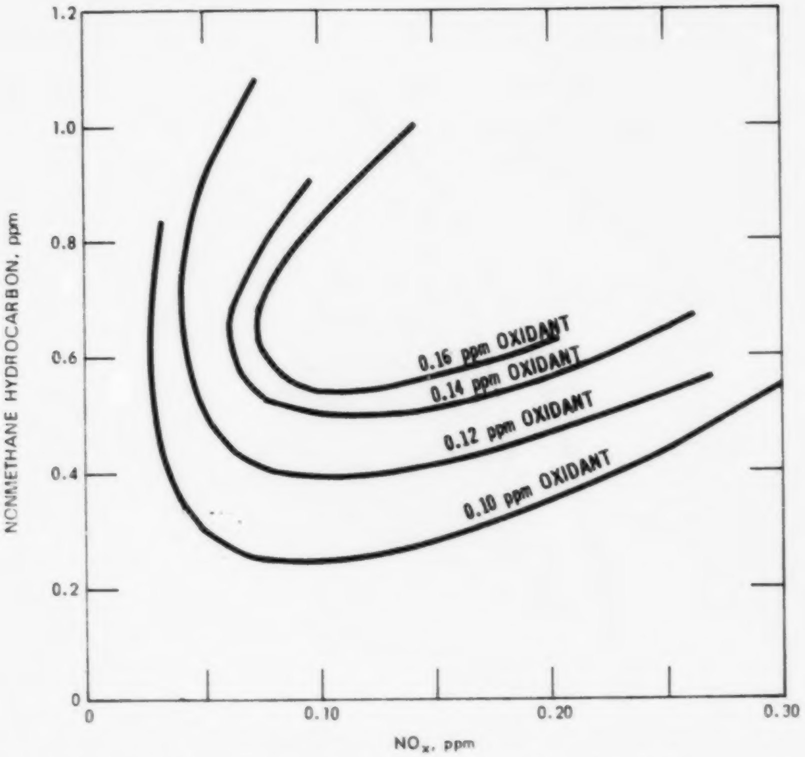

Figure 3-11. Approximate isopleths for selected upper-limit maximum daily 1-hour-average oxidant concentrations, as a function the 6 to 9 a.m. averages of nonmethane hydrocarbons and total nitrogen oxides in Philadelphia, Pa., Washington, D.C., and Denver, Colo., June through August, 1966 through 1968.[24]

The difficulty in establishing the OX-HC-NO relationships from aerometric data alone is understandable if the complexity of these relationships is recognized. Both aerometric data analysis and smog chamber experimentation show clearly that, although the OX varies monotonically with HC, its dependence on NO_x shows a maximum. Further, the OX-HC and OX-NO_x relationships appear to be interdependent; that is,

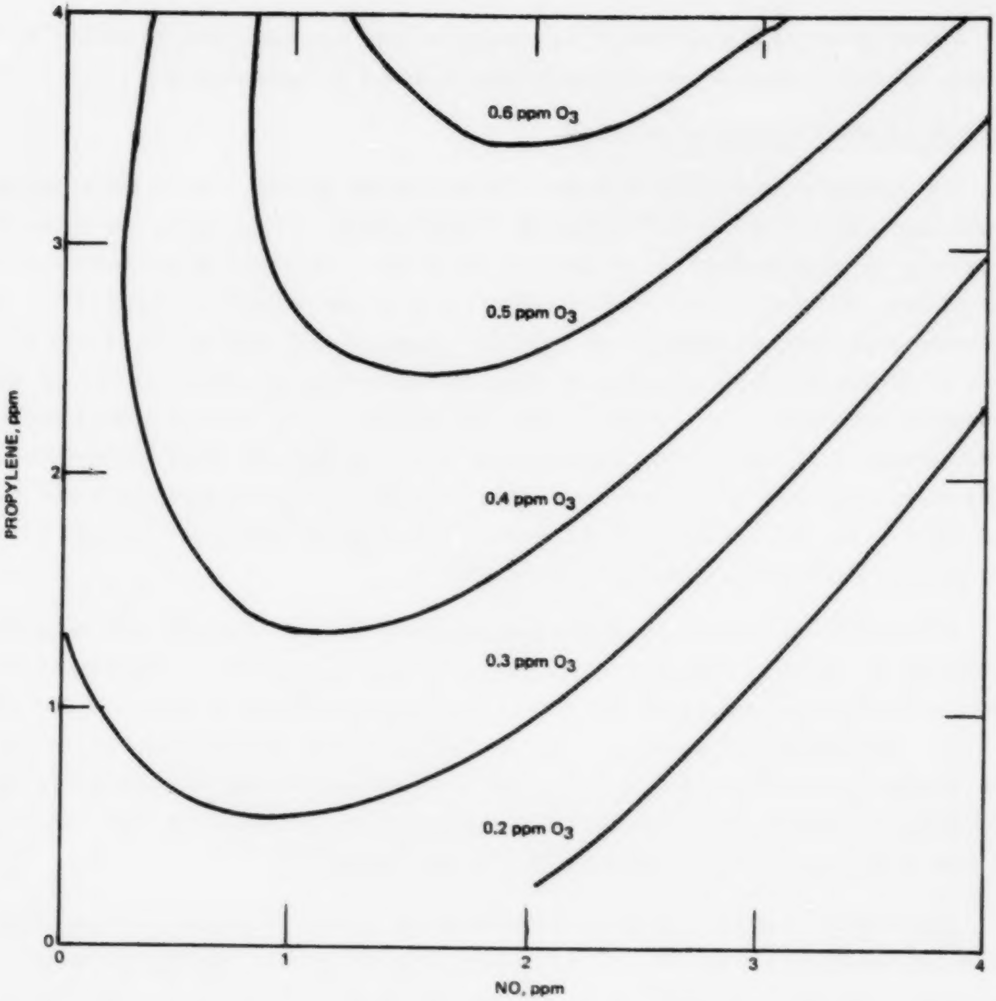

Figure 3-12. Oxidant isopleths from laboratory experiments showing effect of varying initial precursor hydrocarbon (propylene) and nitric oxide concentrations on maximum ozone concentrations.[27]

any relationship of one precursor to oxidant determines, to a degree, the relationship of the other precursor to oxidant. Still another complication is introduced by the apparent fact that the variations of HC and NO_x in ambient air do not parallel each other exactly. Thus, from Figure 3-10 it can be seen that each HC level is associated with a wide range of NO_x values and vice versa.

Because of the uncertainties of the OX-HC-NO_x relationships derived from the presently available aerometric data, the U.S. Environmental Protection Agency (EPA) has judged that use of these relationships to estimate control requirements for oxidant abatement cannot be made with confidence. Instead, EPA elected to use the relatively more accurate OX-NMHC relationship depicted in Figure 3-5 as the basis of the OX abatement strategy now in use in the United States.

A more detailed discussion of the observational approach used to establish the oxidant-oxidant precursor relationships can be found in Reference 24.

Critique of Observational Model

The OX-NMHC relationship (Figure 3-5) arrived at through use of the observational approach clearly is the result of a first effort to delineate the roles of HC and NO_x in OX formation and to provide bases for a rational OX abatement strategy. This effort, although it has probably made the best use of the data available, did not necessarily produce unequivocal results. Some of the limitations of the OX-NMHC curve in Figure 3-5 obviously result from the inaccuracy and insufficiency of the aerometric data available. Other limitations relate to the concept underlying the observational model and become apparent only when the OX-NMHC curve is used to make predictions. In view of the enormous importance of the applications intended for this curve, its limitations--however unavoidable they may be at the present time--must be fully defined, evaluated, and recognized.

The limitations caused by analytical inaccuracies have already been mentioned in Chapter 2. Briefly, the main problems lie in the differential measurement of NMHC and in the measurement of OX in the presence of relatively high levels of NO_x and SO_2. The analytical error in these measurements has a greater effect on the data in the low concentration range. This is a serious limitation because it is the low concentration data that define the air quality standard for NMHC, that is, the NMHC concentration corresponding to the OX standard.

Insufficiency of data also incurs penalty in several respects. First, it does not permit clear and reliable delineation of both the HC and the NO_x roles in OX formation. Second, the shape of the OX-NMHC curve (Figure 3-5) is uncertain, especially in the high concentration range. The magnitude of this latter error is uncertain; however, its direction is known. Because the curve represents the highest OX concentrations ever observed, it follows that the addition of new data points can only raise the curve, resulting in a more linear character. Finally, the insufficiency of data does not permit construction of separate curves for geographical locations with different climatologies. The use of a single OX-NMHC curve to compute control requirements in different regions is obviously inappropriate.

Another persistently criticized limitation of the OX-NMHC curve in Figure 3-5 is that the curve appears to ignore the role of NO_x in OX formation.[28,29] Although this criticism is valid in principle, the magnitude of the limitation is a complex function of several factors, and for this reason the role of NO_x has often been misunderstood.

It should be clear that, except for the uncertainties discussed in the preceding paragraphs, the validity of the existing curve as a depiction of the OX-NMHC relationship is not questioned. Validity questions arise only when this relationship is used to predict the effect of HC control on ambient OX. Such predictions, in order to be valid, require that the OX-NMHC relationship not change as a result of HC control--a requirement that clearly cannot be met because HC control will raise the NO_x-to-HC ratio in air, resulting in a different OX-NMHC relationship.

To better define this conceptual limitation of the OX-NMHC curve, consider its most common application, which is to calculate from OX data alone the degree of HC control required in order to achieve the OX standard. This calculation requires knowledge of (1) the NMHC concentration corresponding to the presently observed OX level, and (2) the NMHC concentration corresponding to the OX standard. Values for both of these entities can be read off the OX-NMHC curve; however, only the former is valid. The value of the NMHC concentration corresponding to the OX standard is probably incorrect because it reflects the present NO_x-to-HC ratio in air rather than the higher ratio that will result from HC control. From smog chamber studies of the OX-HC-NO_x relationships, one may reasonably expect that, under the higher NO_x-to-HC ratio conditions of future atmospheres, the NMHC concentration corresponding to 0.08 ppm of OX (the oxidant standard) will be greater than 0.24 ppm C. Although it cannot be ascertained at this time, a drastically higher NMHC value is not expected. This is because present plans call for control of both HC (to alleviate the OX problem) and NO_x (to alleviate the NO_2 problem). Therefore, a future NO_x-to-HC ratio not drastically higher than the current one would be expected.

A final criticism of Figure 3-5 involves the number and siting of the monitors used to collect the OX and NMHC data. The data were collected at one and the same monitoring site located in the center of the city. The data, therefore, are indicative of the NMHC levels but not of the OX levels because OX is expected to reach its maximum concentration at some point downwind from the emission discharge point.

Smog Chamber Data

Unlike the atmospheric data analysis method, smog chambers provide a simple and practical research tool for studying the HC and NO roles in OX formation. Because experimental conditions in smog chambers can be controlled reliably and at will, smog chamber experimentation is especially useful in studying the chemistry of the OX formation process in detail. Thus, the individual as well as the interactive effects of the precursors HC and NO_x on OX formation can be delineated--a feat practically impossible to accomplish using aerometric data alone. The one--and critical--drawback of the smog chamber method is the limitation in inherent validity that prohibits use of the method for atmospheric predictions. Smog chamber atmospheres are only crude simulations of real atmospheres and, as discussed earlier in this chapter, it is not always possible to test the validity of smog chamber data through comparison with atmospheric data. For these reasons, all early smog chamber findings regarding the OX-HC-NO_x relationships were taken to reflect only qualitatively the relationships existing in the real atmosphere.[27,30-33]

In more recent studies,[23,34,35] the question of comparability of the smog chamber system with the real atmospheric system was given specific attention, and as a result, the OX-HC-NO_x relationships established from these chamber data are believed to have relatively more quantitative validity. These more recent relationships are depicted by the diagrams in Figures 3-13 and 3-14. These diagrams are equal-response lines, each one being the locus of the (NMHC, NO_x) points corresponding to a certain fixed OX concentration. The shaded areas in Figure 3-13 represent those concentrations of the NMHC and NO reactants for which the resultant maximum OX concentration is equal to or less than 0.08 ppm; line "def" represents the NO standard corresponding to the California standard for NO_2 (1-hour average NO_2 concentration not to exceed 0.35 ppm).[34]

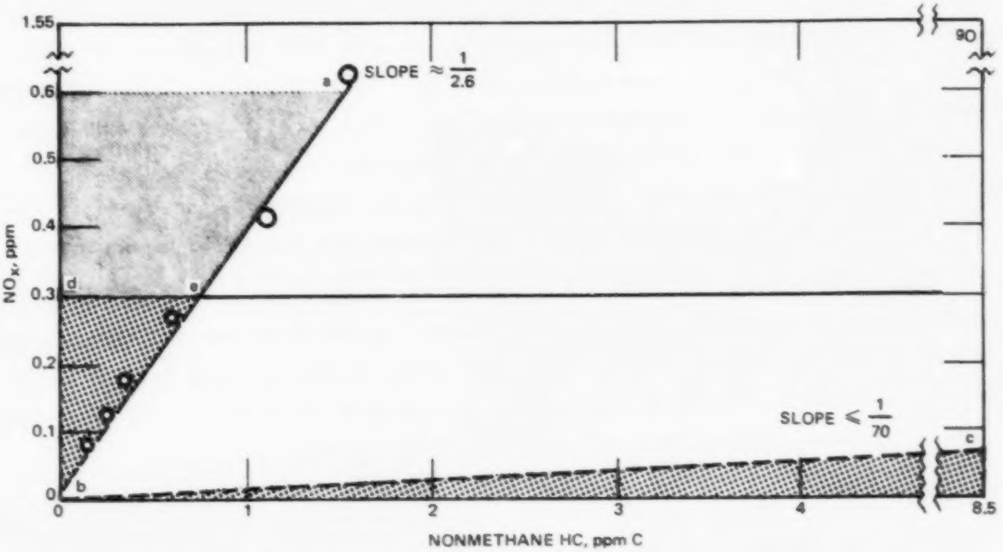

Figure 3-13. Equal response lines representing combinations of total nonmethane hydrocarbon and nitrogen oxide corresponding to oxidant and nitrogen dioxide yields equal to the national air quality standards.[34]

The utility of the information in Figure 3-13 is illustrated in the following example in which a numerical air quality standard for NMHC is calculated using these diagrams. Maximum 6 to 9 a.m. concentrations of NMHC and NO_x during 1970 in the United States--presumed to be those observed in Los Angeles--have been reported to be 8.4 ppm C and 1.4 ppm, respectively (point "g" in Figure 3-13).[29] These concentrations obviously correspond to an OX concentration exceeding the standard. To achieve the OX standard, the NMHC and NO_x levels must be moved from their 1970 position (g) either vertically to below line "bc" or in the direction leading to the "bde" area. Considering the uncertainties regarding the slope of the "bc" line[34]

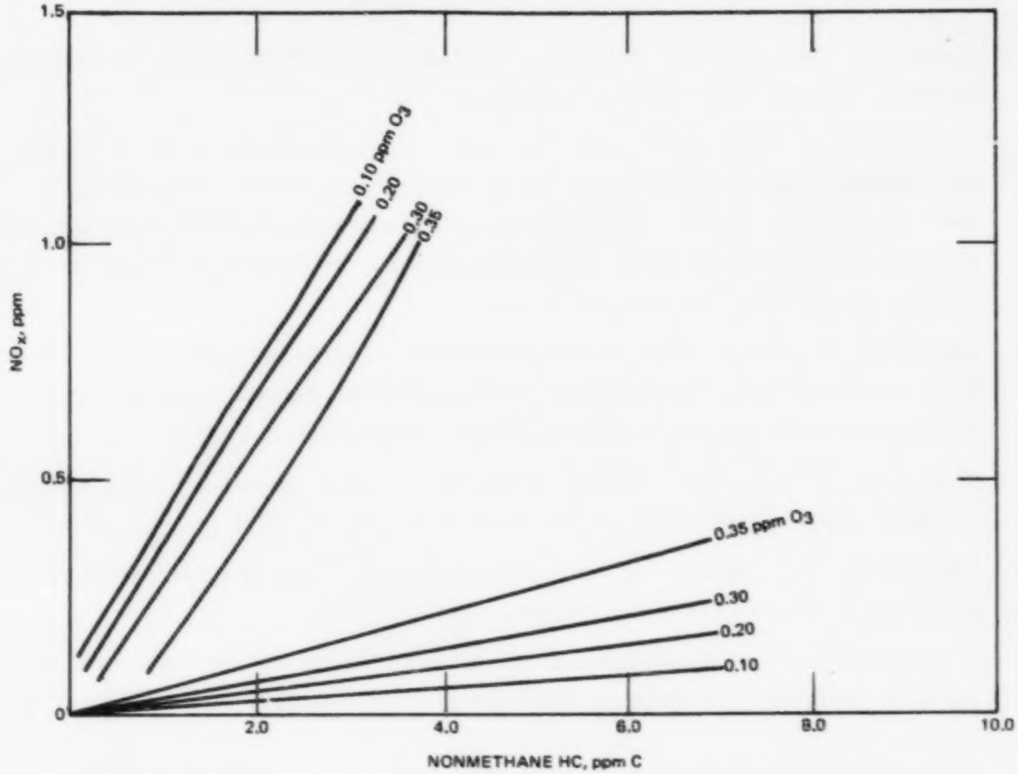

Figure 3-14. Equal response lines representing combinations of total nonmethane hydrocarbon and nitrogen oxide corresponding to specific levels of maximum ozone yields.[34]

and the fact that the NO_x levels below this line are too low to be achieved through a reasonable control effort, it follows that the most rational control is in the direction leading to point e (corresponding to 0.3 ppm NO_x and 0.75 ppm C NMHC). An additional factor to be considered here is the inadvertent variation of the NO_x concentration in the air above a city (Reference 24, Figure 4-7). To understand the effect of this factor, the following facts must be understood: (1) the NO_2 standard imposes an upper limit to ambient NO_x, but not a lower limit, and (2) as illustrated in Figure 3-13, NO_x levels below the "ab" line are associated with above-standard OX levels. Because of these facts and because ambient NO_x levels--corresponding to a constant HC level--vary by as much as +40 percent,[24] it follows that the NMHC must be controlled down to 0.20 to 0.25 ppm C in order to ensure achievement of the OX standard even when the NO_x level is unusually low relative to NMHC.

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CHAPTER 4

EFFECTS OF METEOROLOGICAL FACTORS ON OXIDANT FORMATION

INTRODUCTION

In any given location, the atmospheric concentration of oxidant depends on many factors. Some of these, such as the concentrations of nitrogen oxides and hydrocarbons, and the reactivity of the hydrocarbons, have been mentioned earlier. Other important factors are the size of the area, the meteorology, the topography, the number and distribution of sources, and the rates of emissions.[1-3] These latter factors are important because they affect the distribution of pollution over a city.

The diurnal urban emission pattern of oxidant-forming pollutants is fairly uniform from weekday to weekday. It is apparent, therefore, that variations in the pattern of oxidant concentrations must be caused largely by meteorological factors. Such factors include dilution (accomplished by the same process of atmospheric turbulence and transport that affects other gaseous contaminants), sunlight intensity, and temperature. Moreover, concentrations of oxidant upwind from an area may be substantially different from concentrations downwind as a result of transport phenomena.

Effects from some of these meteorological factors are discussed in the following sections.

EFFECTS OF SUNLIGHT

All photochemical processes in ambient air start with absorption of sunlight by pollutants--those capable of absorbing such light--followed by dissociation into reactive fragments. The most important of these light absorption-dissociation processes involves nitrogen dioxide (NO).

Interaction of light with an NO molecule to form nitric oxide (NO) and an oxygen (O) atom is a reaction between a photon and the NO_2 molecule. Thus, the rate of NO_2 destruction, or of O atom formation, is directly proportional to the intensity of light and the concentration of NO_2. Because ozone (O_3) forms from the reaction of O atoms with molecular oxygen (O_2), it follows that O_3 accumulation depends strongly on light intensity.

The intensity and relative distribution of wavelengths of sunlight reaching the earth's surface does not vary appreciably except in the presence of absorbing species or light-scattering particles. Because polluted atmospheres contain variable amounts of NO_2, and because the NO_2 will absorb certain wavelengths of sunlight, some changes can occur in both the relative wavelength distribution and the intensity of sunlight at a particular location. A reduction as high as 80 percent of intensity near the region of 3250 angstroms (Å) has been observed at the earth's surface during an intense photochemical air pollution episode.[4] Because most of the NO_2 had disappeared from the atmosphere at the time of the episode, it cannot have been responsible for the observed decrease in light intensity. Rather, the reduction has been generally attributed to the light-scattering effect of atmospheric aerosols formed as a by-product of the photochemical interactions of reactive hydrocarbons, nitrogen oxides, and sulfur dioxide.

Light intensity reductions of the magnitude observed would be expected to produce a substantial decrease in the rate of photochemical reactions. The actual effect caused by aerosol diffusion is far more complex, however. As pointed out by Leighton,[5] the available light energy is a function of the mixing height of a given polluted air mass. Within the upper half of the air mass, the available light energy will tend to be the result of aerosol scattering, and this will be substantially greater than that available from incident radiation alone. An opposite effect is observed in the lower half of the air mass. Thus, the formation of photochemical aerosols has the rather interesting effect of increasing the rate of photochemical reactions in the upper half of the polluted air mass and, at the same time, decreasing these rates in the lower half of the air mass. Thus, in areas where visibility is often restricted, a less direct correlation between observed oxidant concentrations and light intensity measured at ground level would be expected. The total effect on oxidant levels of such intensity effects cannot be ascertained without quantitative data on vertical mixing within a polluted air mass.

The variations in sunlight intensity that most affect development of oxidants are those occurring as a function of time of day, time of year, and geographical location. Maximum intensities prevail around noon, with duration times of near-maximum intensities varying according to season and latitude. The amount of cloud cover and the atmospheric accumulation of light-scattering and light-absorbing pollutants are, of course, important factors.

Light intensity and duration control, to some extent, the amount of photo-oxidized materials that can be formed. In the United States, the maximum noonday intensity and the duration of nearly maximum light intensity do not vary appreciably with latitude during the summer months. In the region of 3000 to 4000 Å, the maximum total intensity is 2×10^{16} photons per square centimeter per second (photons cm^{-2} sec^{-1}), with the measurement remaining near this value for 4 to 6 hours.[6] By contrast, the winter values vary from 0.7×10^{16} to 1.5×10^{16} photons cm^{-2} sec^{-1}, depending on latitude; time near maximum light intensity in the winter is reduced to 2 to 4 hours.[6] These times and intensities are important controlling factors in determining the severity and duration of photochemical air pollution.

EFFECTS OF TEMPERATURE AND HUMIDITY

The temperature of a polluted air mass determines the ground state energy of all chemical species in the system. High temperatures increase ground state energy. Because most chemical reactions require addition or subtraction of energy, a temperature variation can also change the reaction rate.

Laboratory experiments[7] have shown that a 40 °F temperature rise increases the rate of NO and hydrocarbon oxidation by a factor of 2. There is also evidence in certain systems that a temperature increase of this magnitude results in a fourfold increase in the rate of oxidant production.[8] These substantial changes can affect the concentrations of photochemical air pollution products in the atmosphere. (At temperatures below 60 °F ambient levels of oxidant seldom exceed a few parts per hundred million.)

Quantitative estimates of the effect of ambient temperature variations upon these manifestations cannot be made at this time. The restrictive nature of the laboratory experiments and the lack of knowledge concerning the variables and reactions involved are two of the factors that prohibit other than qualitative estimates.

The role of humidity in atmospheric reactions and specifically in the oxidant formation process is also extremely complex because humidity may affect oxidant formation both directly and indirectly. Direct effects--namely, acceleration of the NO photooxidation and oxidant formation processes--were reported by Dimitriades;[9] however, the magnitude of these effects has not been established. Humidity also plays an important role in atmospheric aerosol formation; considering the possible destruction of ozone on particulate surfaces, it follows that humidity may also indirectly affect oxidant accumulation.

TRANSPORT PHENOMENA

The transport of pollutants by wind in the Los Angeles basin has been the subject of several studies.[3,10-13] Most of the wind trajectories enter the basin from the west; surface winds are predominately from the ocean to the land during the spring, summer, and fall months.

To illustrate the eastward transport of oxidant, the diurnal variation of mean hourly average concentrations during October 1965 in West Los Angeles, Los Angeles, Azusa, and Riverside are shown in Figure 4-1.[14] Data from the first three stations are from the Los Angeles County Air Pollution Control District; data for the city of Riverside are from the Riverside County Air Pollution Control District.

The station at West Los Angeles is about 10 miles west, and Azusa is about 20 miles east, of downtown Los Angeles. Riverside is about 30 miles east of Azusa.

As shown, the time of the peak oxidant concentrations follows those in West Los Angeles by about 1 hour in Los Angeles, 2 hours in Azusa, and 4 hours in Riverside.

Oxidant concentrations at Riverside exhibited a double peak. The first peak, at about 11 a.m., is attributed to pollutants generated at or near Riverside; the peak at 4 p.m. is attributed to pollutants transported from the large and more densely populated Los Angeles metropolitan area.

As shown in Figure 4-2, the afternoon peak concentration of carbon monoxide in Riverside is much smaller than the morning peak in Los Angeles. This suggests that the polluted air mass was diluted as it moved eastward to Riverside. On the other hand, the afternoon oxidant peak concentrations in Riverside were about as high as the peak concentrations in Los Angeles. It is possible, therefore, that as the polluted air mass moved eastward, the oxidants continued to be formed at a rate about as great as the rate of dilution. It is also just as probable that the second peak at Riverside represents oxidant contributions from local as well as distant sources.

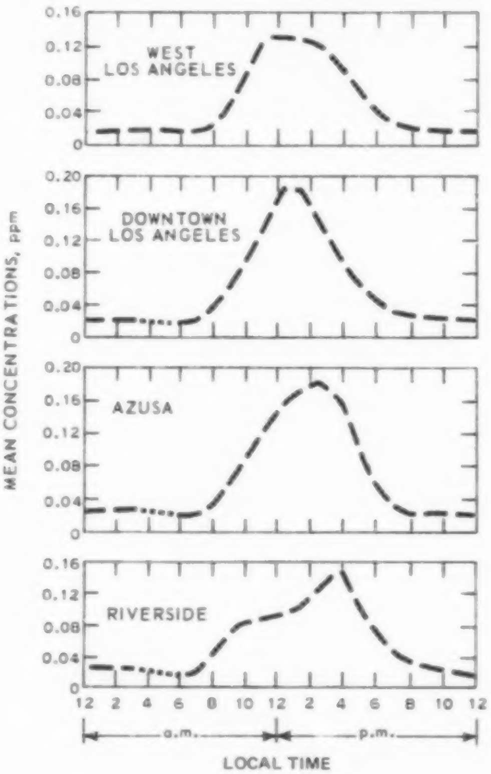

Figure 4-1. Diurnal variation of mean 1-hour average oxidant concentrations at selected California sites, October 1965.[14]

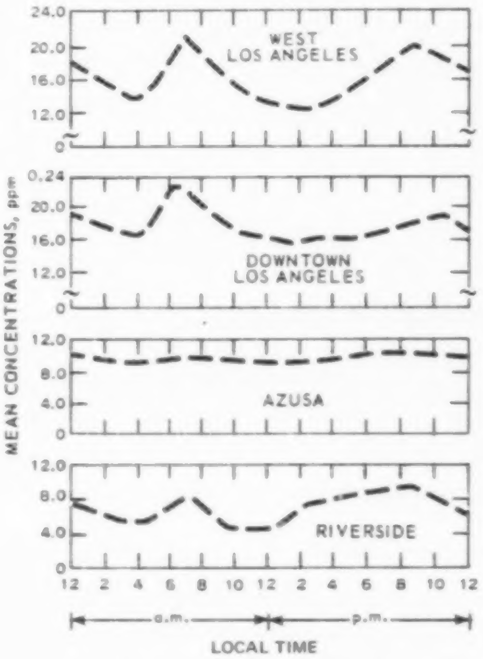

Figure 4-2. Diurnal variation of mean 1-hour average carbon monoxide concentrations at selected California sites, October 1965.[14]

On the average, the direction of flow of surface wind and of pollutant transport appear to coincide, but they are not the only meteorological factors responsible for the transport of pollutants. Bell's appraisal of hour-by-hour development of oxidant concentrations[15] indicates that other mechanisms, such as turbulence and downward motions created mechanically by airflow through mountain gaps, were also responsible for pollutant transport.

On some days, as observed by Stephens,[16] the polluted air mass from the Los Angeles metropolitan area is defined by a sharp boundary that may not extend as far as Riverside. The reason for this sharp boundary, Stephens postulates, is that the temperature profile at the front of the air mass increased to the adiabatic lapse rate resulting in rapid vertical ventilation.

The prevailing winds are not always westerly. Under some meteorological conditions described by Bell,[15] pollutants from Los Angeles have been transported out to sea and then southward to Oceanside[11] and even to San Diego, a distance of over 100 miles. Under other conditions, pollutants have been transported from the sea northward to Ventura and Santa Barbara Counties.[17,18]

Preliminary data from a Statewide Cooperative Air Monitoring Network station recently established by the State of California in Santa Cruz indicate that a similar phenomenon may occur in the region of the San Francisco-Oakland metropolitan area. Under certain conditions, pollutants from the metropolitan area are transported out to sea and then brought back to shore by the local sea breeze to Santa Cruz, about 50 miles south. On these occasions, the hourly average oxidant concentrations have been as high as from 240 to 350 micrograms per cubic meter (0.12 to 0.18 part per million) in Santa Cruz. The very low concentrations of oxides of nitrogen and hydrocarbons measured during these occasions again suggest substantial oxidant formation in spite of high dilution.

FORECASTING TECHNIQUES

Efforts to forecast or estimate future oxidant concentrations have been made for the last 20 years. Initially only the atmospheric dispersion conditions were forecast, then the meteorological forecasts were combined with statistical analysis of past air quality observations to empirically estimate future air quality. The most recent development is the use of numerical models incorporating both meteorological and air quality parameters and processes. An additional simplification that is being tested is the use of regression equations relating the input to the output of each of the specific numerical models.

Air pollution potential forecasting techniques were first developed in the late 1950's and have been considerably improved over the years. The basic product of the air pollution potential forecast is the prediction of the meteorological parameters that affect the transport and diffusion of pollutants. Initially, a stagnation area, in which the conditions for high air pollution potential may develop, must be defined and forecast to continue for at least 36 hours. Then the individual stations within the stagnation area forecast the parameters affecting the pollution potential. The meteorological criteria for a potential air pollution episode at a station are: (1) the morning mixing height must be ≤ 500 meters, (2) the morning transport wind (mean wind within the mixing layer) speed must be ≤ 4 meters per second, (3) the afternoon ventilation (product of the mixing height and transport wind speed) must be ≤ 6000 square meters per second, and (4) the afternoon transport wind must be ≤ 4 meters per second. Air pollution potential forecasts are made and air stagnation advisories are issued regularly by the National Weather Service.

The Los Angeles County Air Pollution Control District uses a combination of meteorological forecasts and past air quality statistics to predict the visibility, eye irritation, and ozone maxima at several stations within the district. Detailed 32- to 36-hour forecasts are made of the meteorological parameters, which are then combined with the ozone statistics. Forecasts of the inversion height, strength, and slope over the Los Angeles basin; the winds over the basin; the maximum temperature; and the cloud cover are prepared. This information is combined with the seasonal variation in hours of sunshine, the monthly station maximum ozone averages, the frequency distributions of monthly station daily maximum ozone values, and the variability of average ozone values by day of the week and holidays. If the predicted ozone concentration equals or exceeds 50 parts per hundred million (pphm), a smog alert is announced.

An evaluation of the Los Angeles data indicates a mean difference between predicted and observed ozone values from May to December of 4.8 pphm. The greatest errors occured in September and October (within the smog season--high ozone values) with differences of 6.7 and 7.0 pphm, respectively. The least errors occurred in December and January (within the relatively smog-free season) with differences of 2.2 and 2.5 pphm, respectively. The most accurate predictions were for the coastal sections, with the error increasing inland.

Recently, numerical models combining the meteorological and photochemical processes have been developed. They are based on the conservation equation. Some are trajectory models and some are Eulerian or grid models. All are first generation efforts and predict the oxidant levels within a factor of 2 or 3. Although the models use observed or predicted meteorological data, the meteorological data are part of the model input. Meteorological prediction models are not, presently, an integral part of the photochemical air quality simulation models. To conserve computer time and storage without affecting the physical assumptions of the model, a linear piecewise regression technique is being evaluated to relate the input and output of a specific model. The numerical modeling effort is in its infancy and much remains to be done.

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CHAPTER 5

ADVERSE EFFECTS OF OXIDANTS

TOXICOLOGIC EFFECTS

The photochemical process produces a number of irritating or toxic chemicals. However, of interest here are only those that are likely to be toxic at or near concentrations found in polluted ambient air. Photochemical oxidants such as ozone, nitrogen dioxide, and peroxyacyl nitrates are gases that exert their toxic influence through exposure by inhalation. If present in sufficient concentrations, these gases are capable of causing death. At sublethal concentrations, they produce more occult but nonetheless health-impairing physiologic malfunctions or anatomic lesions.

Numerous studies of the toxicologic effects of oxidants have been conducted. A detailed review of the data and conclusions from these studies can be found elsewhere.[1] A summarized discussion of these findings is presented in the following sections.

Effects of Ozone

Data from early studies on laboratory animals indicated that death from pulmonary edema and inflammation occurred after exposure to ozone concentrations of 29,400 to 58,000 micrograms per cubic meter ($\mu g/m^3$)--or 15 to 30 parts per million (ppm)--and above for several hours and that pulmonary edema as measured by wet weight to dry weight ratios could be produced by exposures on the order of 1960 to 3920 $\mu g/m^3$ (1 to 2 ppm) for 3 hours in small rodents. Data reviewed here indicate that evidence of transudation of blood protein into the lung (as measured by recovery of labelled albumin in pulmonary lavage fluid) occurs after exposures to as little as 490 $\mu g/m^3$ (0.25 ppm) for a few hours. Cells are quickly damaged and cast off. Regeneration of the same or different cell types is apparent as early as 24 hours after exposure. This is probably not a specific lesion, but is indicative of the presence of a noxious influence at this anatomical level. There is a turnover of cells in the terminal portion of the bronchioles and proximal alveoli, which produces a characteristic lesion consisting of enlarged cuboidal cells (hyperplastic Type II pulmonary epithelium).

A tentative mathematical model for ozone uptake in the respiratory tract of man predicts that the peak dose would occur in the small, but nonterminal, bronchioles (16 to 20th segment of Weible) whose constriction might be expected to lead to decrements in closing capacity measurements. It is of interest in this connection that concomitant exposure to sulfur dioxide and ozone in man causes exaggerated decrements in various pulmonary flow rate responses. However, such response might be predicted from a two-stage action, i.e., proximal airway reflex response for sulfur dioxide and probably ozone plus a second more distal airway direct tissue response for ozone. There appear to be some differences of opinion regarding the segmental level of the most severe airway response on the basis of pathologic anatomy in investigations conducted in laboratory animals: some investigators claim that the most sensitive tissue is in the terminal bronchioles and proximal alveolar epithlium; whereas, others think the higher airway is more sensitive. It is now known, however, that there is fairly diffuse damage throughout the pulmonary portion of the airway. Thus, the mathematical model mentioned above might not necessarily be completely accurate at this tentative stage since allowance for velocity of the bolus of gas at various segmented levels and other factors may need to be adjusted according to more precise pulmonary airway morphometry and experimental observations yet to be made.

As previously mentioned, fibrosis and emphysema are features of exposure to ozone of longer duration, either continuously or intermittently. The role of the epithelial lesion in the genesis of structural modification of the lung is unclear at this time. It may only reflect, for instance, a sequential cycle of epithelial injury and replacement; or, on the other hand, it may be intertwined in some manner with the fibrotic and other changes important in the genesis of emphysema. It is tempting to speculate that the emphysema might be secondary to two independent factors that might act in concert, namely, (1) partial obstruction of the distal airway by the maturation and contraction of the fiborplastic lesions in this region and (2) loss of tone and stretching of the preexisting collagenous pulmonary framework due to chemical alteration of the collagen molecule. Microscopic observations support the fibrosis of the distal airway. A report of the effect of ozone (and nitrogen dioxide) in the denaturation of collagen molecules has been discussed in Reference 1. Increased rigidity occurred principally at edemagenic exposures of ozone and presumably is associated with increased tissue pressure due to fluid or to dilution of the surface-active material by edema fluid. Diminished recoil or elasticity demonstrated by pressure-volume curves employing both air and saline, on the other hand, as noted with repeated exposures to low levels of ozone for 30 days, suggest diminished contractile force of the lung. Furthermore, the animals tested showed gross pulmonary overdistention and a noticeable but, according to the investigators, non-statistically significant reduction in number of alveoli.

It is possible that such changes herald the onset of pulmonary emphysema, which develops at a later stage than elevated expiratory flow resistance. Furthermore, a nonreflex component may be involved. It is possible that the suspected nonreflex component is constriction of the lower airway in response to the direct ozone injury at this segmental level. The recent studies on human volunteers in which closing capacities were studied suggests that this level in the bronchiolar tree contributes significantly to physiologic alterations in human beings and that ozone acts reflexively by stimulating centers in the nasopharynx, thus causing constriction of the larger airways, and nonreflexively by direct chemical action in the terminal portions of the airways.

An interesting feature of acute health response of human beings to ozone exposure has been the apparent augmentation of effects when persons at risk in oxidant episodes indulged in sports. This has shown up in post hoc analysis studies of performance records of high school athletes,[2] and in systematically conducted clinical observations of school children in Japan.[3] A common feature has been that subjects exercising actively suffer higher risk. The observations that human volunteers suffer more decrement in pulmonary physiologic parameters, more mortality due to pulmonary edema,[4] and more susceptibility to pulmonary infection[5] when the subjects exercised during exposure to ozone tend to lend credence to these reports. It would appear fairly reasonable to suppose that the exercise factor produces an increased dose by virtue of increased minute volume. Another factor, however, mouth breathing during strenuous exercise, may be peculiarly important in human exposure; uptake experiments conducted in anesthetized dogs suggest that a change from nose to mouth breathing would double the ozone dose delivered to the deeper airways. While a change from nose to mouth breathing is undoubtedly important in man, this mechanism is not normally resorted to in exercised rodents in which mouth breathing is abnormal. Nonetheless, Stokinger[6] reports a several-fold diminution in the concentration of ozone required to kill rats exposed while exercising. Gardner et al.[5] note an increment in mortality from bacterial infection after ozone exposure of mice while continuously walking.

There appears to be no question that exposure of mice to ozone and synthetic smog at concentrations well below those seen in polluted ambient air enhances mortality from infections. There is, however, a natural reluctance to relate such findings directly to human beings without substantiating evidence in a variety of species. Thus far, in limited studies, considerably higher concentrations of pollutants have been required to effectively show mortality differences in other animals. There is evidence that this may be related to the natural resistance of the animal species to the particular infectious agent rather than to a basic difference in its reactivity to the system. The important point for the successful operation of this system as presently used in animals is the availability of a microorganism that is capable of invading the lung with the subsequent production of mortality. The pollutant then enhances the mortality by depressing the bacterial defense mechanism.

In the application of this model to the human subject through epidemiological studies, it would appear essential to seek associations between oxidant episodes and the establishment of deep lung infection by such pathogens as *Diplococci pneumonia* or *Klebsiells pneumonia*. Such studies have not yet been seriously undertaken.

Effects of Peroxyacetyl Nitrate

Data on the lethality of peroxyacetyl nitrate (PAN) are sparse, but those that are available suggests that it is less lethal to mice than ozone, about the same as nitrogen dioxide, and more lethal than sulfur dioxide.

Campbell et al.[7] exposed mice to high concentrations of PAN, 480 to 700 $\mu g/m^3$ (97 to 145 ppm) as measured at the chamber outlet, for 2 hours at 27°C. The studies demonstrated that the majority of mice exposed to 540 $\mu g/m^3$ (110 ppm) or more of PAN died within a month. It was observed that mice exposed to higher concentrations died earlier than those exposed to lower concentrations. Median lethal exposures characteristically produced a delayed mortality pattern, with most deaths occurring in the second and third week after exposure. Mortality was greater among older mice than younger mice, and it was greater at higher temperatures. It was not influenced appreciably by changes in relative humidity.

Experiments carried out on humans have suggested that exposure to PAN results in increased oxygen uptake during exercise. Smith[8] has carried out a group of studies on male college students averaging 21 years of age. The subjects were exposed to 1485 $\mu g/m^3$ (0.3 ppm) PAN by breathing through the mouth (nose clamps were used) for 5 minutes while at rest, and then the subjects were engaged immediately in 5 minutes of exercise on a bicycle ergotometer. Both air containing PAN and air free of PAN were used without the knowledge of the subjects. Since the pollutant has no characteristic smell or taste, it was considered that the experiment was carried out in a "blind" fashion. It was noted that there was a statistically significant increase in oxygen uptake during exercise, without any change at rest. Expiration velocity was reduced after exercise. The changes could possibly be a reflection of an increase in the work of breathing due to an increase in airway resistance. Because the report of this work does not adequately describe the experimental design or the statistical analysis, these results merit replication before conclusive statements can be made.

In conclusion, the data obtained so far on the effects of PAN on animals and man are too incomplete to enable conclusions to be drawn regarding any effect of this pollutant at ambient concentrations.

EPIDEMIOLOGICAL APPRAISAL OF OXIDANTS

The possibility that photochemical air pollution could be a major health hazard has been of growing concern. A number of systematic studies have been conducted in an attempt to determine if an association exists between episodes of high oxidant pollution and general mortality, acute illness, aggravation of chronic respiratory disease, impairment of performance, or untoward symptoms such as eye irritation. A detailed review of the data and conclusions from these studies can be found elsewhere.[1] A brief summary of these findings follows.

Epidemiologic studies have been conducted to determine the relationship of photochemical air pollution with mortality, hospital admissions, aggravation of respiratory disease, impairment of human performance, irritation of the respiratory tract, and eye irritation. The effects of prolonged oxidant exposure on mortality, morbidity, ventilatory function, and community satisfaction have also been studied.

No convincing relationship was observed between short-term variations in photochemical oxidants and daily mortality or hospital admissions, although there was a suggestion that mortality could be related to oxidant levels.

A study of 137 patients with asthma demonstrated significantly more asthma attacks on days when maximal hourly photochemical oxidant concentrations exceeded 430 $\mu g/m^3$ (0.25 ppm).

Chronic respiratory disease patients who were removed from an ambient atmosphere of elevated oxidant concentrations to a room from which pollutants were filtered have shown improvement in ventilatory function. In two other studies, no significant association was found between variations in ambient oxidant levels and changes in respiratory symptoms or function in patients with chronic respiratory disease.

The team performance of high school cross-country track runners was impaired on days of elevated oxidant concentrations measured 1 hour before the commencement of each race; hourly oxidant concentrations ranged from 60 to 590 $\mu g/m^3$ (0.03 to 0.3 ppm). The threshold for this effect has subsequently been estimated at about 235 $\mu g/m^3$ (0.12 ppm). These findings may possibly be related to a pulmonary irritation effect similar to that shown to occur at higher levels of exposure but at lower levels of exertion. Significantly more automobile accidents have also occurred on days of high oxidant concentrations.

A study of student nurses in Los Angeles has demonstrated a threshold for increased cough and chest discomfort at daily maximum hourly average oxidant concentrations between 500 and 600 $\mu g/m^3$ (0.25 and 0.30 ppm). This same study also indicated a threshold for increased eye discomfort on days with maximum hourly average oxidant concentrations at about 300 $\mu g/m^3$ (0.15 ppm). These results are consistent with those from other studies that have shown that eye irritation appears to increase when oxidant concentrations exceed 200 $\mu g/m^3$ (0.10 ppm).

Eye irritation, at times accompanied by nasal irritation, was the most frequently reported nuisance effect of air pollution in California. A postulated explanation for the relationship between ambient oxidant levels and eye irritation is that the level of oxidant is a measure of the photochemical activity that produced the eye irritants. The relationship between oxidants and eye irritation is discussed in more detail later in this chapter.

Lung cancer mortality rates were similar among California residents studied in both high- and low-oxidant-pollution areas. A relationship between noncancerous chronic respiratory disease mortality and long-term photochemical oxidant exposure has been suggested in an isolated study in which other important variables were not analyzed. Factors other than oxidant exposure could well have accounted for these observations, and considerable documentation from other epidemiologic studies is required to substantiate these findings. Several surveys have also reported a higher incidence of both chronic respiratory disease symptoms and other respiratory symptoms, including asthma and nose and throat complaints, among residents of Los Angeles than among residents of other areas of California.

A significantly larger proportion of Los Angeles residents have been subjectively bothered by air pollution than have residents of the San Francisco Bay area and the rest of the state. A larger proportion of residents who were bothered by air pollution have considered moving or have moved from Los Angeles than have residents of other areas of California. One-third of the physicians sampled in the Los Angeles area had advised one or more of their patients to leave the area for health reasons, and nearly one-third of the physicians had themselves considered moving from Los Angeles because of air pollution.

In conclusion, from the information presently available, it appears that epidemiologic evidence on the health effects of photochemical oxidant pollution is inadequate. Consistent results for some effects, obtained by various investigators under varying conditions of exposure, are lacking. The few demonstrated associations between oxidant exposure and health effects, such as asthma, pulmonary function, or athletic performance, are inadequate to establish with confidence minimum threshold levels for each effect.

Reported studies suggest, however, that photochemical oxidants are potentially hazardous environmental contaminants. Subjects with chronic respiratory disease seem to be those most threatened by such exposure, but virtually all segments of the population may experience eye irritation at levels of oxidants frequently present in the ambient air. Hazards to normal respiratory function, optimum athletic performance, and safe automobile driving have also been suggested. An association, although not necessarily a cause-effect relationship, has been shown to exist between ambient levels of photochemical oxidants and eye irritation. Since one of the objectives of air pollution control is to promote good health and minimize exposures to potentially hazardous pollutants, the information provided by reported studies cannot be discounted.

CORRELATION OF OXIDANT WITH EYE IRRITATION

Several studies have been conducted in Los Angeles to determine the occasions and the types of pollutants responsible for eye irritation and their relationship, if any, to oxidant pollution. The first set of studies was conducted by the Air Pollution Foundation in 1954.[9]

During the first period of the study, observers were asked on Tuesdays and Fridays to report eye irritation. This later was changed to just those days for which eye-irritating levels of pollution were predicted. In general, the observers were office and factory workers; one of the panels consisted of a group of staff members of the California Institute of Technology. The eye irritation data were compared with instantaneous values of oxidant concentrations as measured by potassium iodide analyzer. The resultant data are shown in Figures 5-1 and 5-2.[10] The "expert" panel (experienced scientists) and the other panel did not significantly differ in the correlations of eye irritation with oxidants, carbon monoxide, particulates, and aldehydes. During the second period, August through November of 1955, similar panels observed eye irritation effects during each day of the work week. In this study, maximum oxidant concentrations were compared with reported eye irritation effects.

The data from these studies demonstrate increasing eye irritation with increasing concentrations of oxidant pollution over the range of instantaneous values from 100 to 880 $\mu g/m^3$ (0.05 to 0.45 ppm), although no clearly demarcated threshold level for this effect is apparent (see Figure 5-1).

Other studies on eye irritation have been performed, including one in which a panel of employees of the Los Angeles County Air Pollution Control District was questioned during the period 1955-1958.[11] A group of environmental sanitation workers in the San Francisco Bay area was also studied during the same period. Neither of these panels reported anything other than a tendency to experience increasing occurrence of eye irritation with increasing oxidant levels. As in all such studies, some individuals reported eye irritation even when no oxidant was present.

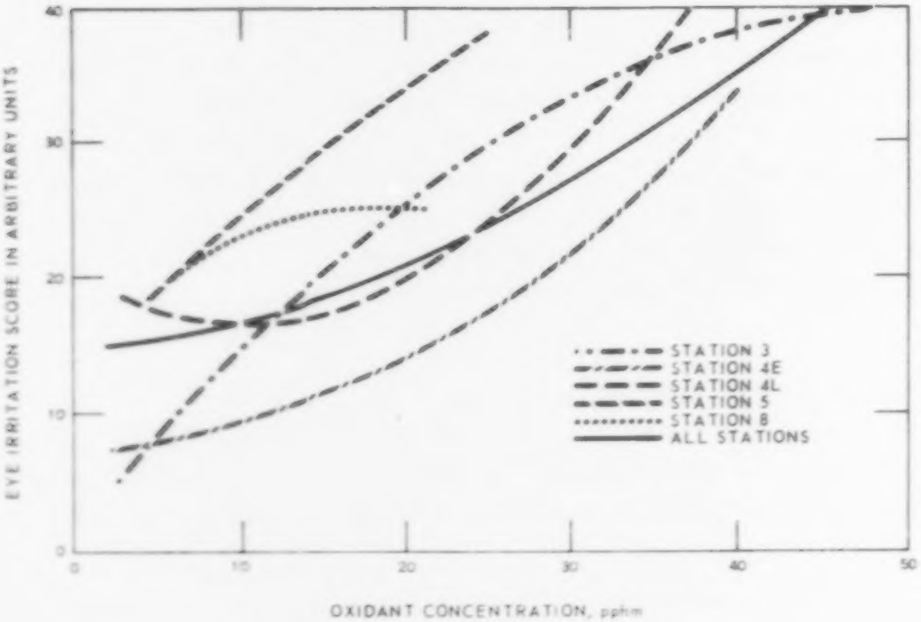

Figure 5-1. Regression curves relating eye irritation and simultaneous oxidant concentrations from a number of stations in the Los Angeles area.[10]

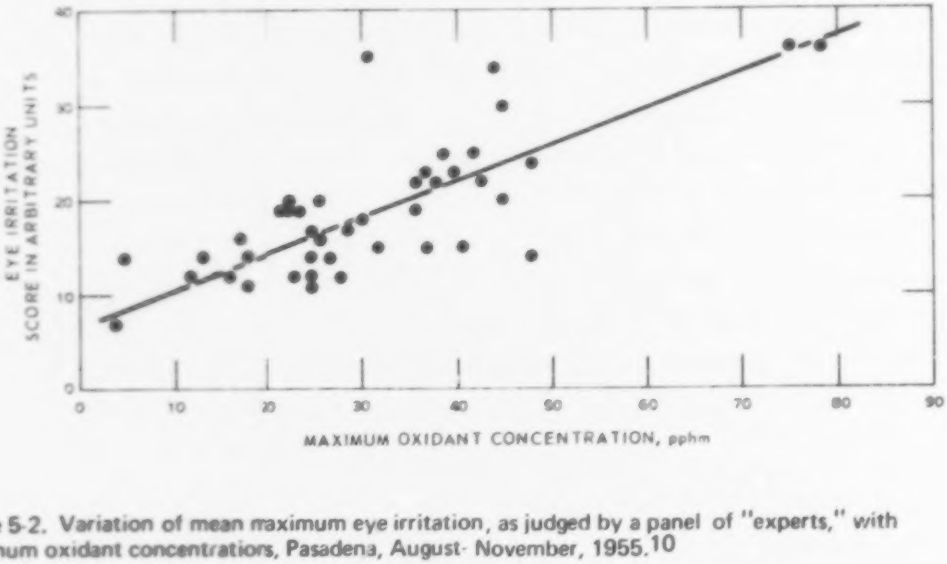

Figure 5-2. Variation of mean maximum eye irritation, as judged by a panel of "experts," with maximum oxidant concentrations, Pasadena, August- November, 1955.[10]

Hammer et al.[12] reported on respiratory and eye symptoms among two groups of student nurses studied during a 24-day period from October 29 through November 25, 1962, in Santa Barbara and Los Angeles. Data plotted in Figure 5-3 again show a relationship between increasing eye irritation and maximum daily photochemical oxidant concentrations over the range of 200 to 800 μg/m^3 (0.10 to 0.55 ppm).

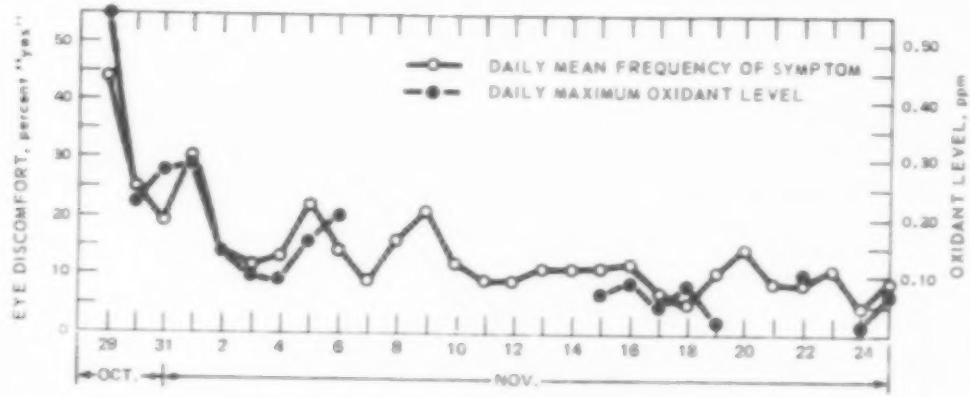

Figure 5-3. Relationship between oxidant concentrations and eye discomfort in Los Angeles, October 29 through November 25, 1962.[10]

A study was conducted to evaluate the sensory effectiveness of air-filter media for removing eye irritants from polluted air in downtown Los Angeles.[13] A statistically significant correlation between eye irritation and oxidant concentrations was found to occur in nonfiltered room air. The scatter diagram of results (Figure 5-4) suggests an eye irritation threshold as the concentration of oxidants exceeds 200 μg/m^3 (0.10 ppm). The index of eye irritation for the study groups increased progressively as oxidant concentrations exceeded the 200 μg/m^3 (0.10 ppm) level.

Oxidant measurements at levels likely to be associated with eye irritation have been reported for a number of cities outside California. Circumstantial evidence of increased eye irritation has been reported in Washington, D. C., Denver, New York City, and St. Louis. An epidemiologic study of eye irritation was carried out by McCarroll et al.[14] on a population living in midtown Manhattan. In October 1963, substantial increases occurred in the frequency of new reports of eye irritation (increasing from about 2 to nearly 5 percent of the population). Oxidant measurements, made at some distance away, had increased during the period under study. Unfortunately, clear conclusions from these data cannot be drawn; there were high levels of sulfur oxide pollution, of particulate pollution, and of carbon monoxide. It is quite possible that eye irritation symptoms in New York City result from mixed pollution of both the oxidizing and reducing type.

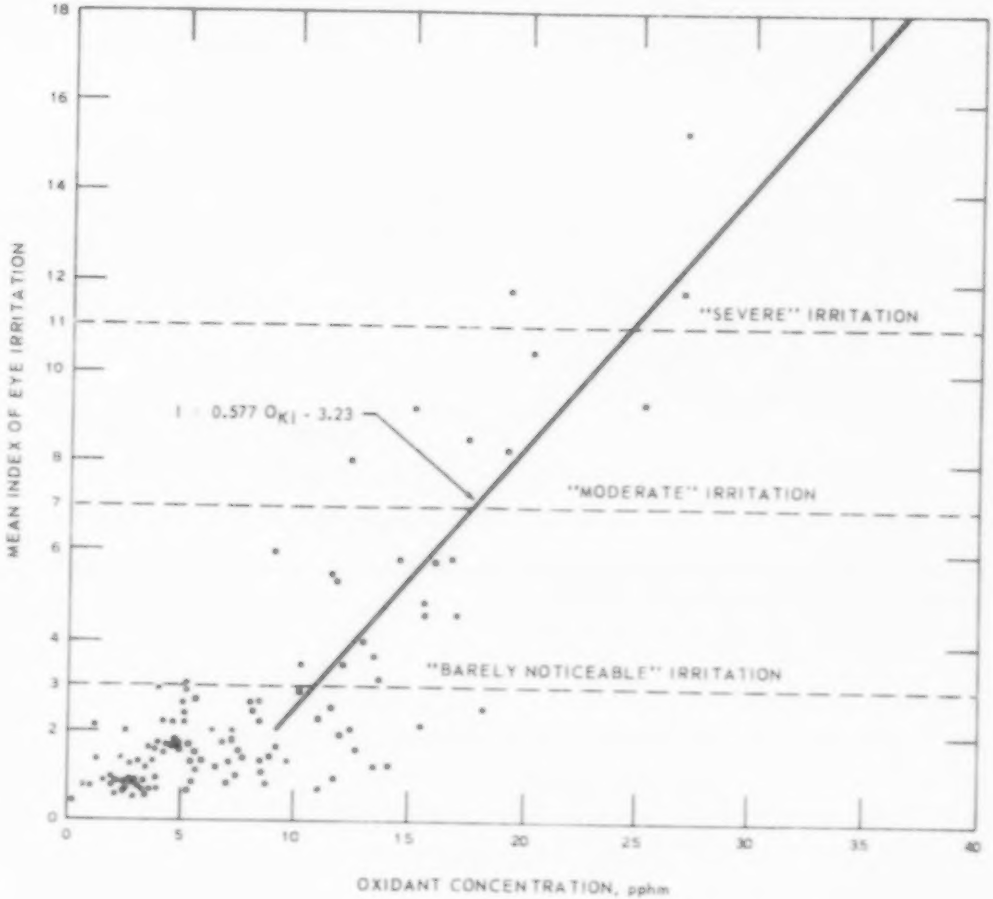

Figure 5-4. Mean index of eye irritation versus oxidant concentration.10

It should be noted here that when interpreting implied relationships associating eye irritation and ambient oxidant levels, care must be exercised in conclusions regarding cause and effect. Experimental studies have shown that ozone, the principal contributor to ambient oxidant levels, is not an eye irritant. Peroxyacyl nitrates have been shown to be powerful eye irritants; even more irritating is peroxybenzoyl nitrate. Formaldehyde and acrolein, also products of the photochemical system, have been shown to produce eye irritation. A postulated explanation for the relationship between ambient oxidant levels and eye irritation is that "oxidant" is a measure of the photochemical activity that produces the aforementioned eye irritants.

EFFECTS OF OXIDANTS ON VEGETATION

Introduction

Injury to vegetation was one of the earliest manifestations of photochemical air pollution. A peculiar type of injury to leafy vegetables, ornamentals, and field crops, characterized by banding, silvering, and stippling of the leaves, was first investigated in the United States by Middleton et al.[1] Plant injury of this kind has since spread to widely separated areas of the world, with increasing severity and with associated economic losses to both farmers and nurserymen.

Three specific phytotoxic materials have been isolated from the photochemical complex: ozone, nitrogen dioxide, and the peroxyacyl nitrates. The latter homologous series of compounds includes peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), peroxybutyryl nitrate (PBN), and peroxyisobutyryl nitrate ($P_{iso}BN$). Preliminary work has shown that PPN is several times as toxic to vegetation as PAN while PBN and $P_{iso}BN$ are more toxic than PPN. Since PAN is the only member of the series that has received much study, and since PPN and PBN, though usually present in the ambient air, are normally below detectable limits, discussion will be restricted to the effects of PAN.

The presentation of the quantitative effects of ozone and PAN has to be limited to laboratory and controlled field exposures since, under ambient conditions, the effects of these compounds cannot be easily differentiated. The term "oxidant" will be used when discussing the toxic materials to which the plants are exposed under ambient conditions. Research has shown that additional phytotoxicants may be present in the photochemical complex. Synergistic effects between the toxicants discussed and other atmospheric contaminants may also produce injury to sensitive plant species. On the basis of available information, ozone is the most important phytotoxicant of the photochemical complex.

A detailed review of the studies conducted in the United States and the resultant evidence can be found elsewhere.[1] Following is a brief summary of the findings.

Review of Information on Effects

Acute symptoms are generally characteristic of a specific pollutant while chronic injury patterns are not. Injury to leaves by ozone is identified as a stippling or flecking. Such injury has occurred experimentally in the most sensitive species after exposure to 60 $\mu g/m^3$ (0.03 ppm) ozone for 8 hours. Injury will occur in shorter time periods when low levels of sulfur dioxide are present. PAN-produced injury is characterized by an under-surface glazing or bronzing of the leaf. Such injury has occurred experimentally in the most sensitive species after exposure to 50 $\mu g/m^3$ (0.01 ppm) PAN for 5 hours. Leaf injury has occurred in certain sensitive species after a 4-hour exposure to 100 $\mu g/m^3$ (0.05 ppm) of total oxidant.

There are a number of factors affecting the response of vegetation to photochemical air pollutants. Variability in response is known to exist between species of a given genus and between varieties within a given species. Sensitive plants can be useful biological indicators of photochemical air pollution. Varietal variations have been most extensively studied with tobacco, and a sensitive tobacco strain, Bel-W3, has been isolated and developed as a monitor for studying the extent, severity, and frequency of ambient oxidant.

The influence of light intensity on the sensitivity of plants during growth appears to depend on the phytotoxicant. Plants are more sensitive to ozone when grown under low light intensities. Reported findings are in general agreement that sensitivity of greenhouse-grown plants to oxidants increases with temperature from 4.4° to 32.7°C (40° to 100°F). However, there is some indication that this positive correlation may result from the overriding influence of light intensity on sensitivity.

The effects of humidity on the sensitivity of plants has not been well documented. General trends indicate that plants grown and/or exposed under high humidities are more sensitive than those grown at low humidities. Though there has been little research in this direction, there are indications that soil factors influence the sensitivity of plants to phytotoxic air pollutants. Plants grown under drought conditions are less susceptible than those grown under moist conditions. Studies indicate that plants appear to be more sensitive when they are grown in soil having low total fertility.

The age of the leaf under exposure is important in determining its sensitivity to air pollutants. There is some evidence that oxidant or ozone injury may be reduced by pretreatment with the toxicant.

Identification of an injury to a plant as being caused by air pollution is an arduous undertaking. Even when the markings on the leaves of a plant can be identified with an air pollutant, it is often quite difficult to evaluate these markings in terms of their effect on the intact plant. Further difficulty arises in trying to evaluate the economic impact of air pollution damage to the plant.

The interrelations of time and concentration, or dose, as they affect injury to plants, are essential to air quality criteria. There are, however, only scant data relating concentrations and length of photochemical oxidant exposure to chronic injury and effects on reduction of plant growth, yield, or quality. There is also a dearth of information relating acute injury to concentrations and duration of exposure to PAN or mixtures of photochemical oxidants. A larger body of information exists on the acute effects of ozone, but even in this instance, the information is far from complete.

Bacteriostatic and bacteriocidal properties of photochemical oxidants in general have been demonstrated. The growth suppression of microorganisms by ozone is a well-known phenomenon, although ozone concentrations for this activity are undesirable from a human standpoint. The bacteriocidal activity of ozone varies with its concentration, the relative humidity, and the species of bacteria.

Hydrocarbons were first recognized as phytotoxic air pollutants about the turn of the century as a result of complaints of injury to greenhouse plants from illuminating gas. Ethylene was shown to be the injurious component. Renewed interest in hydrocarbons, and ethylene in particular, occurred in the mid-1950's when ethylene was found to be one of the primary pollutants in the photochemical reaction complex. Research on several unsaturated and saturated hydrocarbons proved that only ethylene had adverse effects at known ambient concentrations. It is noteworthy that the activity of acetylene and propylene resemble more closely that of ethylene than do other similar gases, but 60 to 500 times the concentration is needed for comparable effects.

In the absence of any other symptom, the principal effect of ethylene is to inhibit growth of plants. Unfortunately, this effect does not characterize ethylene because other pollutants at sublethal dosages, as well as some diseases and environmental factors, may also inhibit growth.

Epinasty of leaves and abscission of leaves, flower buds, and flowers are somewhat more typical of the effects of ethylene, but the same effects may be associated with nutritional imbalance, disease, or early senescence. Perhaps the most characteristic effects are the dry sepal wilt of orchids and the closing of carnation flowers. Injury to sensitive plants has been reported after exposure to ethylene concentrations of 1.15 to 575 $\mu g/m^3$ (0.001 to 0.5 ppm) for an 8- to 24-hour period.

Economic loss has not been widely documented except among flower growers in California, where damage to orchids and carnations has been assessed at about $800,000 annually. More research needs to be done on economic losses sustained in field and greenhouse crops from long exposures to very low concentrations of ethylene.

EFFECTS OF OXIDANTS ON MATERIALS

Studies have focussed mainly on the effects of ozone and nitrogen dioxide on materials. A detailed discussion of the symptoms and mechanism of ozone and nitrogen dioxide attack on materials can be found elsewhere.[1] The following paragraphs summarize the information relative to the effects of ozone on materials presented in Reference 1.

Ozone is a major factor in the overall deterioration of a number of different types of organic materials. In fact, certain specific organic compounds are more sensitive to ozone attack than humans or animals. The magnitude of damage is difficult to assess in some cases because naturally occurring ozone is a component of weathering, and weathering itself is a major cause of materials deterioration. Nevertheless, researchers have shown that atmospheric ozone resulting from the activities of man has been responsible for accelerating the deterioration of several classes of materials.

Although the total extent of ozone-associated damage to materials is not known, ozone may very well be a major contributor to the weathering of materials. Ozone is an extremely active compound, and generally, any organic material is incompatible with concentrated ozone. Many organic polymers are subject to chemical alteration from exposure to very small concentrations of ozone, including atmospheric concentrations. This sensitivity usually increases with the number of double bonds in the chemical structure of the polymer.

The most widely used generic groups of elastomers are highly sensitive to attack by atmospheric ozone. These groups include natural rubber and synthetic polymers of styrene-butadiene, polybutadiene, and polyisoprene. Atmospheric ozone will not attack vulnerable elastomers exposed in a relaxed state (no stress) even for long periods of time. However, cracks easily develop on exposure to atmospheres containing 20 to 40 $\mu g/m^3$ (0.01 to 0.02 ppm) ozone if vulnerable elastomers are under a tensile stress of as little as 2 or 3 percent. Unfortunately, elastomeric products are normally used in a stressed state. Other factors that determine the rate of ozone attack on elastomers are the type and formulation of the elastomeric material, concentration of atmospheric ozone, period of exposure, rate of diffusion of ozone to the elastomer surface, and temperature.

Researchers have developed antiozonant additives that are capable of protecting elastomers from ozone attack. Antiozonants, however, are expensive and sometimes migrate to the surface of elastomeric products, where they may be removed during usage. Oils, gasoline, and other chemicals may extract antiozonants from elastomers and thus decrease the resistance to ozone attack.

Researchers have conducted laboratory exposures of textiles to ozone. Apparently only cotton is affected. Considering the above-normal exposure concentrations and the limited end-use life of most cotton products, the magnitude of deterioration by ozone is minimal.

Some important textile dyes, however, are susceptible to fading during exposure to ozone. Certain blue disperse dyes used on acetate and polyester/cotton fabrics and nylon carpets have been particularly troublesome. Laboratory exposures have shown that ozone concentrations as low as 100 $\mu g/m^3$ (0.05 ppm) are capable of producing visible fading. To prevent or mitigate fading by ozone, the textile industry can select combinations of fabrics, resistant dyes, and inhibitors, but these increase the cost of finished products.

Laboratory exposures of different types of paint have shown some damage with exposure to ozone at 1960 $\mu g/m^3$ (1.0 ppm), but essentially no statistically detectable damage when exposed to concentrations of 196 $\mu g/m^3$ (0.1 ppm). Oil-based house paint was most susceptible. Field exposures in Los Angeles (high smog pollution) also produced considerably more damage to some paints (especially the oil-based house paint) than was observed at a rural control exposure site.

A recent atmospheric corrosion study indicates that the presence of oxidants (mainly ozone) inhibits the corrosion rates of several types of common steels. Increasing oxidant concentrations correlate with decreasing corrosion rates, even when atmospheric sulfur dioxide is present.

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CHAPTER 6
ATMOSPHERIC LEVELS AND VARIATION OF OXIDANT PRECURSORS AND RELATED POLLUTANTS

INTRODUCTION

It has been established unequivocally that the oxidants found in urban atmospheres are secondary pollutants and that the primary pollutants that act as oxidant precursors are the hydrocarbons and the nitrogen oxides, i.e., nitric oxide and nitrogen dioxide (NO and NO_2). To be more accurate, not all atmospheric hydrocarbons are capable of producing oxidants--methane being the most important exception--and there are nonhydrocarbon organics also (e.g. aldehydes) that are capable of forming oxidant. However, as a first approximation, the term "hydrocarbons," or better yet "nonmethane hydrocarbons," adequately describes the organic component of the oxidant precursor mixture in the atmosphere.

Because of this reactant-product relationship between oxidant and the oxidant precursors, any oxidant abatement strategy must rely exclusively on modification of the atmospheric concentrations of the precursors. For this reason, knowledge of the concentrations of oxidant precursors and of the oxidant-oxidant precursor association in the ambient air is essential. Such information has been obtained in the United States and is presented here. Data on concentrations and concentration variation patterns for the oxidant precursors are presented and discussed in this chapter. The subject of the quantitative relationships between oxidant and oxidant precursors, being extremely complex and somewhat controversial, is treated rigorously in a separate chapter. Data on ambient sulfur oxides and aerosol are also included in this chapter, mainly for the purpose of providing a more complete picture of the pollutants that may have a role in the oxidant formation process.

CONCENTRATIONS OF HYDROCARBONS IN URBAN ATMOSPHERES

Analytical Methods

The data available on atmospheric concentrations of hydrocarbons were obtained primarily by three analytical methods: flame ionization detection (FID), gas chromatography (GC) coupled with FID, and infrared spectrophotometry applied either in a scanning or the nondispersive mode. Mass spectrometry, colorimetry, and coulometry were also used but to a much lesser extent.

The FID instruments respond to organic compounds with an intensity that is approximately in proportion to the number of carbon atoms bound to carbon or hydrogen. Carbon atoms bound to oxygen, nitrogen, or halogens cause reduced or no response. Since the FID response per carbon atom is not exactly the same from compound to compound, FID measurement results are usually expressed in terms of parts per million of the calibration gas used. For example, a measurement result of 10 ppm-methane (or 10 ppm C) means that the analyzed sample caused a response equal to that caused by 10 parts per million of methane. Thus, for samples with substantially different hydrocarbon compositions, the FID readings may not accurately reflect differences in total hydrocarbon concentration among the samples.

FID has been used in conjunction with subtractive columns to make measurements upon fractionated hydrocarbon mixtures. Thus, to measure the methane and total nonmethane hydrocarbon levels in air, the U.S. Environmental Protection Agency's Continuous Air Monitoring Program (CAMP) stations used FID and a carbon column that could selectively remove all nonmethane hydrocarbons from a sample. Similar techniques were also used in some special studies to collectively measure the following hydrocarbon groups: (1) olefins and acetylenes; (2) aromatics except benzene; and (3) the other hydrocarbons in the sample, including benzene.

Such fractionations and associated measurements upon the ambient hydrocarbon mixture are extremely useful for reasons that are discussed in more detail in the next section. Briefly stated here, the reason is that such fractionations provide simple and practical means of excluding hydrocarbons that do not contribute appreciably to photochemical oxidant from the hydrocarbon measurement. The most noteworthy application of such a technique is in the monitoring of total nonmethane hydrocarbon. Considering the predominately natural origin, high relative levels, and extremely low reactivity of methane, measurement of nonmethane hydrocarbons provides a much more accurate measure of the controllable organic precursors of oxidant than measurement of total hydrocarbon.

Gas chromatography coupled with FID was used to obtain whatever data are presently available on the detailed composition of atmospheric hydrocarbons. Unfortunately, the amount of these extremely useful data obtained thus far is very limited, mainly because of the high demands of the chromatographic method in time, skill, and expense.

Nature and Concentrations of Hydrocarbons in Urban Atmospheres

Although on occasions all other hydrocarbon concentrations drop to unmeasurably low levels, methane does not. Numerous measurements[1] suggest a worldwide minimum methane concentration of about 0.8 to 1.0 mg/m^3 (1.2 to 1.5 ppm). In inhabited areas, methane levels are often much higher; values of 4 mg/m^3 (6 ppm) or more have been observed.[2]

Ratios of nonmethane hydrocarbons (as carbon) to methane have been estimated for urban areas, after subtracting the background levels of methane.[2]

The nonmethane to methane hydrocarbon ratios for several weeks averaged 0.6 in Cincinnati, Ohio, and 1.9 in Los Angeles, California, although methane values were similar (Figure 6-1). The higher Los Angeles ratios are probably caused by greater traffic density, solvent losses, and natural gas emissions in that area.

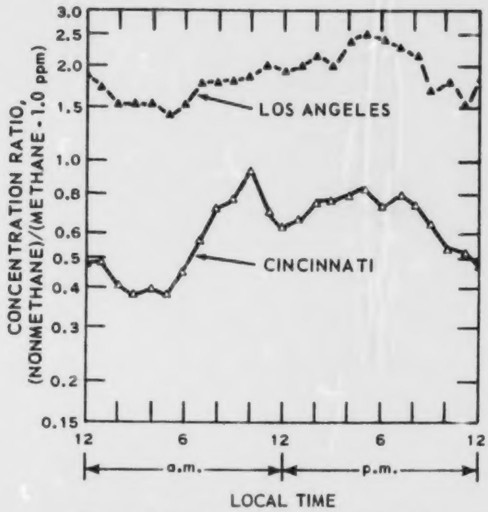

Figure 6-1. Concentration ratios for nonmethane hydrocarbons/methane in Los Angeles (213 hours during October and November 1964) and Cincinnati (574 hours during September 1964), with 655 μg/m3 (1 ppm) methane deducted to correct for estimated background biospheric concentration.[2]

Table 6-1 lists the individual hydrocarbons detected in samples of urban air by gas chromatographic analysis in several investigations.[3-5] Of the 56 compounds detected, 17 were alkanes, 23 were alkenes (including two alkadienes), 2 were alkynes, 10 were aromatics, 3 were cycloalkanes, and 1 was a cycloalkene. The length of this list is limited only by the sensitivity of the analytical methods, and it is certain that many additional hydrocarbon compounds are actually present in urban air. Especially at the higher carbon numbers, the chromatographic data become so complex that their interpretation in terms of individual compounds may be highly uncertain. The listing in Table 6-1 of compounds with carbon numbers of 7 and higher must be considered as only a partial list.

All the hydrocarbons above carbon number 4 listed in Table 6-1 are found in gasoline.[6] These and the lower alkenes and acetylenes are also found in automobile exhaust gases. The lower alkanes (methane, ethane, and propane) occur in only small amounts in auto exhaust gases, but are ordinary constituents of natural gas. Stephens and Burleson[3] have reported that the hydrocarbon composition of Los Angeles air resembled that of auto exhaust gases with an addition

Table 6-1. SOME HYDROCARBONS IDENTIFIED IN AMBIENT AIR[3-5]

Carbon number	Compound	Carbon number	Compound
1	Methane	6	Hexane
			2-methylpentane
			3-methylpentane
2	Ethane		2,2-dimethylbutane
	Ethylene		2,3-dimethylbutane
	Acetylene		
			cis-2-hexene
3	Propane		*trans*-2-hexene
	Propylene		*cis*-3-hexene
	Propadiene		*trans*-3-hexene
	Methylacetylene		2-methyl-1-pentene
			4-methyl-1-pentene
			4-methyl-2-pentene
4	Butane		Benzene
	Isobutane		Cyclohexane
	1-butene		Methylcyclopentane
	cis-2-butene		
	trans-2-butene	7	2-methylhexane
	Isobutene		3-methylhexane
	1,3-butadiene		2,3-dimethylpentane
			2,4-dimethylpentane
			Toluene
5	Pentane		
	Isopentane	8	2,2,4-trimethylpentane
	1-pentene		*o*-xylene
	cis-2-pentene		*m*-xylene
	trans-2-pentene		*p*-xylene
	2-methyl-1-butene	9	*m*-ethyltoluene
	2-methyl-2-butene		*p*-ethyltoluene
	3-methyl-1-butene		1,2,4-trimethylbenzene
	2-methyl-1,3-butadiene		1,3,5-trimethylbenzene
	Cyclopentane		
	Cyclopentene	10	*sec*-butylbenzene

of natural gas and gasoline vapor. However, samples taken in industrial areas and from near the smoke plume from a brush fire have shown distinctive differences in composition, which should reasonably be attributed to these particular recognized sources.

Some total hydrocarbon concentration data for California are given in Table 6-2.[7] Since interest here is only in the oxidant-forming potential of hydrocarbons, the data in Table 6-2 are of limited utility for two reasons: first, because they include methane, which is not an oxidant precursor; and second, because they represent hydrocarbon concentrations observed at an unspecified time of the day. Insofar as oxidant formation is concerned, hydrocarbon data mainly of interest are only those for the reactive--that is, oxidant-forming--hydrocarbons, and for the concentrations of such hydrocarbons during the morning hours, e.g., 6 to 9 a.m. only. After 9 a.m., hydrocarbon concentrations are generally

Table 6-2. MEAN OF DAILY MAXIMUM HOURLY AVERAGE TOTAL HYDROCARBON CONCENTRATIONS FOR 17 CALIFORNIA CITIES, 1968-1969[7]
(ppmC)

City	1968							1969				
	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
San Francisco Bay Area												
Richmond	5	6	4	6	9[a]	8	9[a]	8	8	7	6	4
San Rafael	4	4	5	6	13[a]	10	9	6	6	8	6	6
San Francisco	5	4	N.A.[b]	5	7[a]	6	6	5	5	5	5	4
Redwood City	N.A.	12	14	16[a]	13	11	9	7	6	7	5	5
San Jose	4	4	4	6	8[a]	8[a]	7	7	5	6	6	5
Central Valley												
Fresno	3	3	3	4	6[a]	5	5	4	4	5	3	3
Bakersfield	7	7	8	10[a]	10[a]	9	10[a]	7	8	7	6	6
Sacramento	4	4	5	5	10[a]	7	7	6	5	7	4	4
Stockton	3	4	4	5	6[a]	4	5	4	3	5	4	4
Central Coast												
Salinas	3	2	3	3	3	4[a]	4[a]	3	3	3	2	N.A.
Monterey	3	2	3	3	4[a]	4[a]	4[a]	4[a]	4[a]	3	3	3
Southern California												
Los Angeles (downtown)	4	5	4	5	6	7[a]	7[a]	6	4	5	4	3
Azusa	4	4	5	5	6[a]	5	5	4	4	5	5	5
Anaheim	4	5	5	6	8	10[a]	10[a]	7	7	7	5	3
Riverside	5	5	7	6	7	7	8	7	9[a]	8	4	4
San Bernardino	4	5	5	6[a]	6[a]	6[a]	6[a]	5	N.A.	6[a]	5	4
San Diego	3	N.A.	4	5	7	7	9[a]	7	6	6	5	3

[a] Highest mean concentration for 12-month period.
[b] N.A. = not available.

smaller and participate to a lesser extent in the oxidant-forming process. Also, hydrocarbon concentrations during the summer and early fall months are of relatively greater interest because it is during these months that atmospheric oxidant reaches its highest concentration levels in the year.

Frequency distribution data for 6 to 9 a.m. nonmethane hydrocarbon concentrations in various cities are given in Table 6-3. It should be noted that nonmethane hydrocarbon concentration is determined as difference between a total hydrocarbon measurement and a methane measurement. Therefore, the analytical error attendant to the nonmethane hydrocarbon determination is relatively large, suggesting that measurements of concentrations below 0.1 ppm C are unreliable.

Seasonal and Diurnal Variation

Data available have not been analyzed yet for seasonal variations in nonmethane hydrocarbon levels. In 14 of the 17 California cities included in Table 6-2, the highest hydrocarbon concentrations occurred in October or November. Such consistency is presumably a consequence of the generally similar meteorological conditions along the California coast. Cities elsewhere would be expected to show other patterns, dependent on their particular meteorology.

Table 6-3. FREQUENCY DISTRIBUTION DATA FOR 6 TO 9 a.m. NONMETHANE HYDROCARBON CONCENTRATIONS AT CAMP SITES, 1967-1972

(ppm C)

Site	Year	Number of samples	Min.	Percentile[a]									Max.	Arithmetic		Geometric	
				10	20	30	40	50	60	70	80	90		Mean	Standard deviation	Mean	Standard deviation
Denver, Colorado (060580002A10)	67[b]	29	0.0	0.0	0.3	0.4	0.6	0.9	1.1	1.8	2.3	2.7	5.2	1.3	1.2	0.74	3.69
	68[b]	161	0.0	0.2	0.4	0.6	0.8	1.0	1.1	1.4	1.7	2.7	5.3	1.2	1.0	0.87	2.62
	69[b]	219	0.0	0.0	0.1	0.3	0.5	0.7	0.8	1.0	1.3	1.7	4.9	0.8	0.8	0.50	3.26
	70[b]	231	0.0	0.0	0.2	0.3	0.5	0.6	0.8	1.0	1.1	1.6	5.9	0.8	0.7	0.52	2.96
	71[b]	178	0.0	0.3	0.6	0.7	0.9	1.1	1.3	1.5	1.8	2.4	5.7	1.3	0.9	0.99	2.29
	72	282	0.0	0.1	0.4	0.5	0.7	0.9	1.1	1.3	1.6	2.0	3.9	1.0	0.7	0.74	2.73
Washington, D.C. (090020002A10)	66[b]	250	0.0	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	1.0	1.8	0.5	0.3	0.35	2.56
	68[b]	244	0.0	0.0	0.1	0.1	0.3	0.4	0.5	0.6	0.8	1.1	2.6	0.5	0.4	0.35	2.73
	69[b]	231	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.3	0.5	2.3	0.2	0.2	0.15	2.27
	70[b]	267	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.5	0.8	2.0	0.3	0.3	0.19	2.62
	71	279	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.3	0.5	0.8	3.3	0.3	0.3	0.20	2.64
	72[b]	187	0.0	0.0	0.0	0.0	0.1	0.2	0.3	0.5	0.6	1.1	2.0	0.4	0.4	0.25	2.82
Chicago, Illinois (141220002A10)	68[b]	146	0.0	0.1	0.2	0.4	0.6	0.8	1.0	1.1	1.4	1.8	2.8	0.8	0.6	0.64	2.58
	69	300	0.0	0.0	0.1	0.3	0.5	0.7	0.8	1.1	1.4	1.8	3.6	0.8	0.7	0.54	2.99
	70[b]	220	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.5	0.9	1.4	4.1	0.5	0.7	0.25	3.20
	71[b]	269	0.0	0.0	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.4	2.7	0.6	0.5	0.46	2.58
Philadelphia, Pennsylvania (397140002A10)	66[b]	142	0.0	0.0	0.3	0.5	0.6	0.7	0.8	1.1	1.4	1.7	4.2	0.9	0.7	0.64	2.70
	67[b]	260	0.0	0.0	0.1	0.2	0.3	0.5	0.6	0.8	1.1	1.6	5.9	0.7	0.7	0.42	3.11
	68[b]	154	0.0	0.0	0.0	0.1	0.2	0.3	0.5	0.6	0.9	1.6	3.7	0.6	0.7	0.34	3.17
	69[b]	192	0.0	0.0	0.1	0.2	0.3	0.5	0.6	0.7	0.9	1.3	3.7	0.6	0.5	0.42	2.74
	70[b]	2.64	0.0	0.0	0.1	0.2	0.3	0.4	0.6	0.7	1.0	1.3	2.3	0.5	0.4	0.37	2.90
	71[b]	234	0.0	0.0	0.0	0.1	0.2	0.2	0.4	0.4	0.6	0.9	3.0	0.4	0.4	0.27	2.74
	72[b]	59	0.0	0.0	0.0	0.1	0.3	0.4	0.4	0.6	0.7	1.1	2.4	0.5	0.4	0.31	3.02
Cincinnati, Ohio (361220003A10)	68[b]	109	0.0	0.0	0.0	0.1	0.2	0.3	0.4	0.6	0.8	1.4	3.4	0.5	0.6	0.31	3.18
	69[b]	188	0.0	0.0	0.0	0.2	0.2	0.4	0.4	0.5	0.7	1.1	3.1	0.5	0.5	0.32	2.79
	70[b]	99	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.4	2.3	0.1	0.3	0.12	2.22
	71[b]	104	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.9	1.1	2.0	0.6	0.4	0.45	2.37
	72[b]	238	0.0	0.1	0.2	0.3	0.3	0.4	0.4	0.5	0.7	1.0	3.4	0.5	0.4	0.40	2.09
St. Louis, Missouri (264280002A10)	68[b]	198	0.0	0.0	0.0	0.2	0.4	0.6	0.8	0.9	1.1	1.6	4.4	0.7	0.7	0.44	3.25
	69	292	0.0	0.0	0.1	0.2	0.3	0.4	0.5	0.7	1.0	1.4	3.4	0.5	0.5	0.37	2.83
	70[b]	232	0.0	0.0	0.0	0.1	0.2	0.3	0.4	0.6	0.7	1.1	2.9	0.4	0.4	0.31	2.72
	71	3.4	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.3	0.4	0.7	2.5	0.2	0.3	0.19	2.54
	72[b]	235	0.0	0.0	0.0	0.0	0.1	0.2	0.2	0.3	0.4	0.7	1.8	0.3	0.2	0.21	2.42

[a] Concentrations greater than or equal to specified value in indicated percentage of samples.

[b] Yearly standard exceeded.

Figures 6-2 and 6-3 show diurnal patterns for nonmethane hydrocarbons in several cities, averaged over several months.[8,9] In most of these, the maximum concentrations at 6 to 8 a.m. are mainly due to the morning commuter traffic rush. The morning peak is clearest in Denver and Los Angeles, where the automobile is especially important as a means of transportation. However, even within a large metropolitan area, there may be considerable variation. Figure 6-3 shows average diurnal patterns for nonmethane hydrocarbons at three locations in Los Angeles County. There are considerable differences among the three patterns, although the morning maxima are still evident in all. Table 6-4 gives diurnal patterns for the C_2 to C_4 hydrocarbons and isopentane, showing the hour-by-hour variations as averaged over several weeks in the Los Angeles smog season. All species listed reach a maximum in the morning, then decline through the midday.[10]

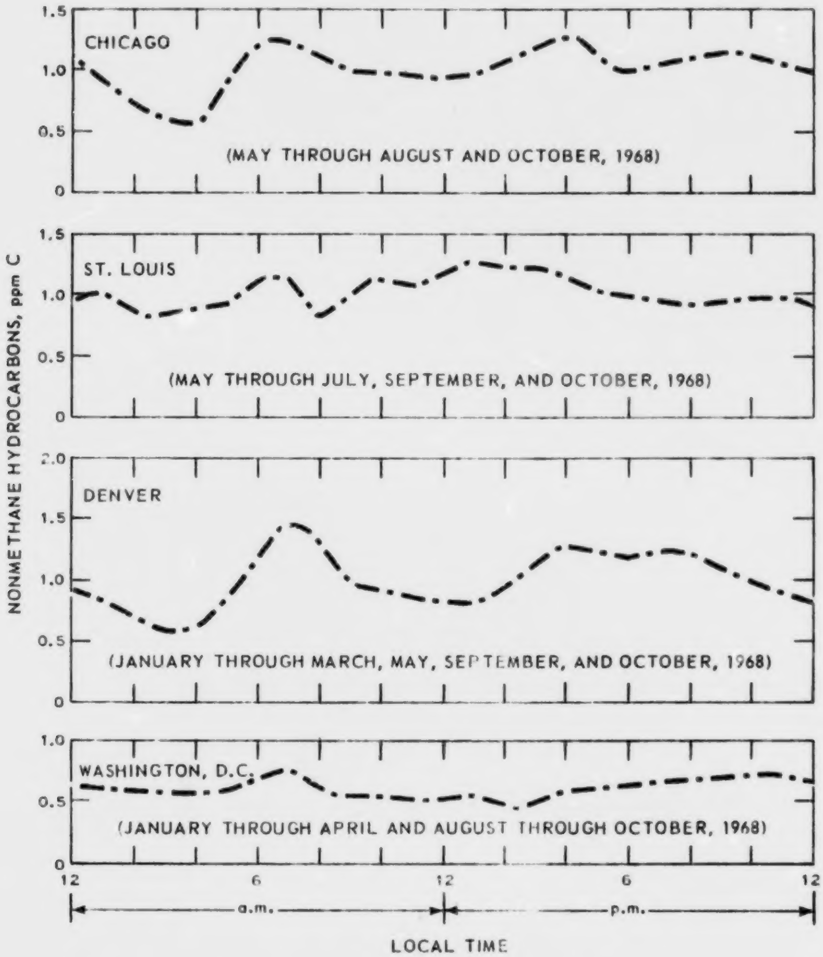

Figure 6-2. Nonmethane hydrocarbons by flame ionization analyzer, averaged by hour of day over several months for various cities.[8]

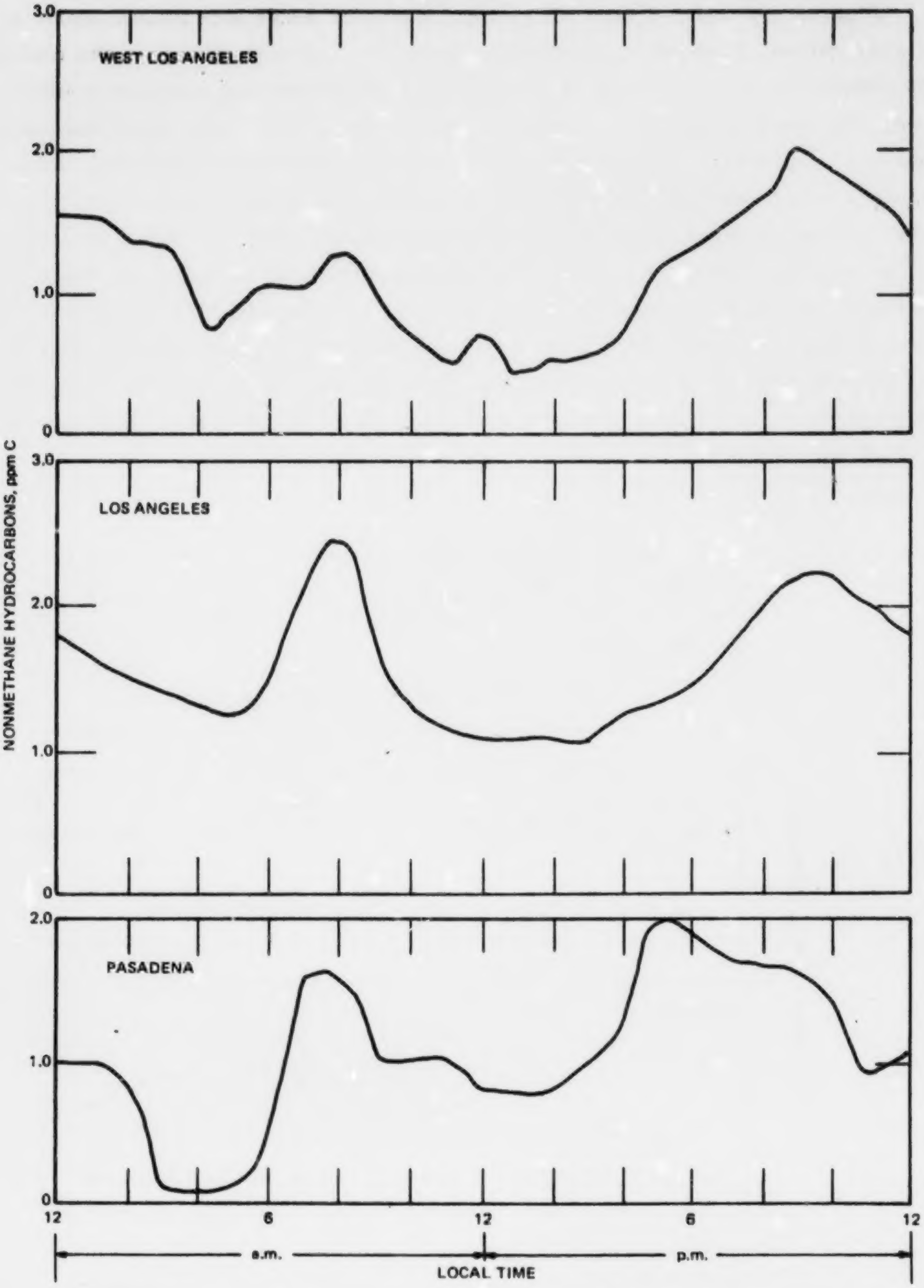

Figure 6-3. Nonmethane hydrocarbons by flame ionization analyzer averaged by hour of day for three Los Angeles County sites, October 1966 through February 1967.[9]

Hydrocarbon Trends

As with the oxidant trends, the hydrocarbon trends discussed here are those observed in the Los Angeles air basin, for which the atmospheric data available are abundant.[11] Such data consist of total hydrocarbon measurements

Table 6-4. AVERAGE ATMOSPHERIC LIGHT HYDROCARBON CONCENTRATIONS, BY HOUR, LOS ANGELES AND AZUSA, SEPTEMBER THROUGH NOVEMBER, 1967[10]
(ppm C)

Location	Local time	Days averaged	Ethane	Ethylene	Acetylene	Propane	Propylene	Isobutane	n-butane	Butylenes	Isopentane
Downtown Los Angeles	5 a.m.	27	0.140	0.031	0.077	0.113	0.025	0.053	0.176	0.032	0.177
	6	28	0.140	0.049	0.112	0.113	0.036	0.061	0.200	0.034	0.224
	7	28	0.151	0.122	0.234	0.125	0.064	0.074	0.300	0.056	0.335
	8	31	0.145	0.102	0.212	0.126	0.054	0.075	0.304	0.049	0.346
	9	15	0.107	0.063	0.141	0.098	0.032	0.063	0.209	0.028	0.249
	10	33	0.126	0.067	0.152	0.118	0.038	0.064	0.260	0.034	0.303
	11	12	0.094	0.039	0.106	0.080	0.025	0.048	0.180	0.021	0.200
	12 noon	32	0.106	0.039	0.101	0.108	0.020	0.063	0.200	0.015	0.199
	1 p.m.	16	0.076	0.020	0.068	0.078	0.013	0.044	0.149	0.014	0.162
	2	38	0.094	0.026	0.074	0.097	0.017	0.057	0.156	0.019	0.155
	3	16	0.090	0.026	0.079	0.101	0.016	0.050	0.132	0.020	0.144
	4	34	0.075	0.036	0.095	0.081	0.024	0.046	0.139	0.021	0.141
East San Gabriel Valley (Azusa)	5 a.m.	32	0.143	0.029	0.060	0.087	0.013	0.036	0.101	0.014	0.104
	6	33	0.128	0.017	0.065	0.076	0.015	0.031	0.098	0.012	0.103
	7	30	0.180	0.030	0.103	0.102	0.024	0.041	0.136	0.018	0.144
	8	32	0.118	0.037	0.101	0.084	0.020	0.044	0.149	0.018	0.160
	9	18	0.093	0.031	0.079	0.065	0.015	0.036	0.114	0.015	0.114
	10	32	0.086	0.024	0.069	0.066	0.019	0.040	0.132	0.015	0.136
	11	18	0.090	0.021	0.057	0.062	0.011	0.037	0.107	0.010	0.101
	12 noon	30	0.089	0.015	0.050	0.058	0.010	0.040	0.098	0.009	0.093
	1 p.m.	16	0.111	0.016	0.066	0.067	0.018	0.046	0.121	0.017	0.111
	2	42	0.097	0.018	0.064	0.075	0.017	0.050	0.121	0.018	0.117
	3	16	0.092	0.020	0.065	0.075	0.015	0.081	0.175	0.015	0.125
	4	37	0.079	0.021	0.058	0.076	0.014	0.041	0.122	0.014	0.123

and were taken from 11 monitoring stations operated during most of the period 1963-1972. The data are presented in Tables 6-5 through 6-7, using the following presentation forms:

1. The average of maximum hourly concentrations during July, August, and September (an average of 92 values each year).
2. The average concentrations from 6 to 9 a.m. during July, August, and September (an average of 276 one-hour values each year).
3. The annual average of maximum hourly concentrations (an average of 365 values each year).

Table 6-5. TOTAL HYDROCARBON TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF DAILY MAXIMUM ONE-HOUR CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a,11]
(ppm C)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	--	6.9(2)	5.7	6.1	4.8	5.0	5.0	5.3	6.1	6.6
Azusa	4.9	4.5	--	--	3.8(2)	4.7	5.9	7.8	5.9	5.5
Burbank	6.4	4.9	--	--	--	--	--	6.1	5.9	5.2
Lennox	--	--	--	--	--	--	--	5.8	4.5	4.8
Long Beach	5.6	5.9	5.6	6.0	--	--	--	--	--	--
Los Angeles, Downtown	6.3	4.4	6.9(1)	6.0	4.6	4.5	4.8	5.0	4.8	4.6
Pasadena	--	--	--	--	4.4	4.9	3.9	3.2	4.2	4.5
Pomona	--	--	--	--	--	--	--	4.1	3.5	3.5
Reseda	--	--	--	--	--	--	--	5.4	4.2	4.4
Riverside	--	6.3(2)	6.0	5.9	5.2	4.7	5.3	5.6	4.6	4.2
San Bernardino	--	--	5.3	5.8	5.2	5.2	5.3	5.4	4.8	4.7

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Table 6-6. TOTAL HYDROCARBON TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF 6 TO 9 a.m. DAILY AVERAGE CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a,11]
(ppm C)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	--	4.9(2)	4.1	4.2	3.8	3.5	4.0	3.9	5.1	4.6
Azusa	3.8	3.3	--	--	--	3.4	4.4	5.1	4.2	4.0
Burbank	5.0	4.2	--	--	--	--	--	5.0	5.0	4.2
Lennox	--	--	--	--	--	--	--	4.3	3.2	3.2
Long Beach	4.4	4.5	4.3	4.5	--	--	--	--	--	--
Los Angeles, Downtown	5.6	3.7	5.7	5.4	4.2	3.9	3.9	4.4	4.4	4.1
Pasadena	--	--	--	--	3.7	4.1	3.0	2.5	3.5	3.5
Pomona	--	--	--	--	--	--	--	3.4	3.0	3.0
Reseda	--	--	--	--	--	--	--	3.8	3.6	3.6
Riverside	--	5.2(2)	4.5	4.9	4.3	3.9	4.6	4.2	3.9	2.9
San Bernardino	--	--	4.5	4.8	4.5	4.3	4.4	4.8	4.0	4.0

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Table 6-7. TOTAL HYDROCARBON TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, ANNUAL AVERAGES OF DAILY MAXIMUM ONE-HOUR CONCENTRATIONS FOR ALL DAYS OF THE YEAR[a,11]

(ppm C)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	--	$8.3^{(8)}$	6.8	7.3	6.9	6.9	5.9	6.3	6.9	7.6
Azusa	4.4	4.1	$4.6^{(7)}$	--	$4.6^{(8)}$	4.6	5.0	6.0	5.5	5.4
Burbank	7.5	6.5	$7.3^{(7)}$	--	--	--	--	$7.3^{(5)}$	7.3	7.0
Lennox	--	--	--	$9.9^{(10)}$	--	--	--	$6.9^{(4)}$	6.8	6.6
Long Beach	$7.8^{(6)}$	7.1	7.9	$6.9^{(3)}$	--	--	--	--	--	--
Los Angeles, Downtown	7.1	6.1	$6.4^{(1)}$	6.3	5.3	5.2	4.7	5.1	5.2	4.8
Pasadena	--	--	--	$6.9^{(9)}$	5.2	5.3	4.1	4.1	4.5	5.1
Pomona	--	--	--	--	--	--	--	$4.4^{(4)}$	4.2	4.1
Reseda	--	--	--	--	--	--	--	$6.4^{(5)}$	5.4	5.5
Riverside	--	$7.2^{(8)}$	6.0	6.8	5.5	5.8	$5.5^{(2)}$	5.6	5.0	5.4
San Bernardino	--	$7.6^{(10)}$	5.0	5.8	5.6	5.4	5.1	5.2	4.9	5.1

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Nonmethane hydrocarbon data computed from the total hydrocarbon data using established relations between total and nonmethane hydrocarbon for the Los Angeles atmosphere are depicted in Figure 6-4. Figure 6-5 shows trends of the 6 to 9 a.m. nonmethane hydrocarbon in Los Angeles, along with corresponding trends of the 6 to 9 a.m. nitrogen oxides and the maximum hourly oxidant. Figure 6-6 shows distribution of total hydrocarbon concentrations in the Los Angeles air basin.

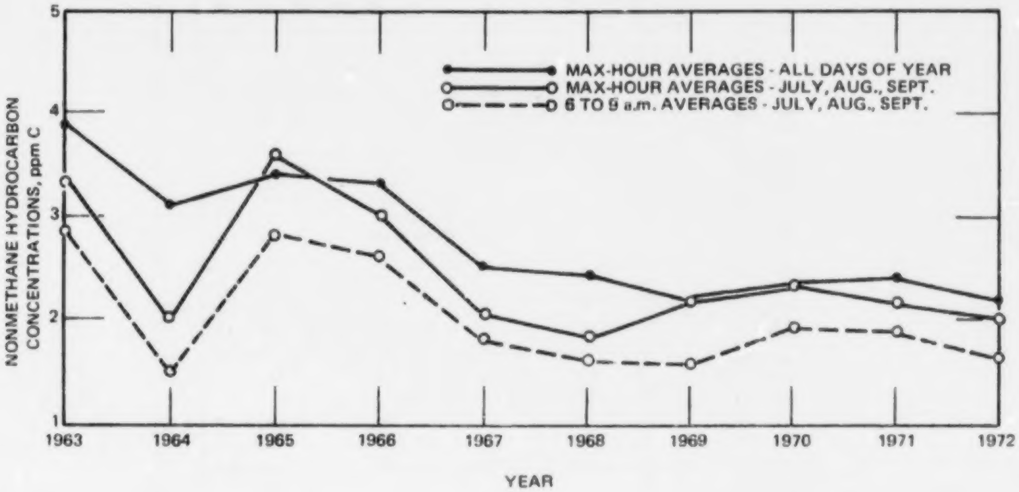

Figure 6-4. Nonmethane hydrocarbon trends in Los Angeles, 1963-1972.[11]

CONCENTRATIONS OF NITROGEN OXIDES IN URBAN ATMOSPHERES

The nitrogen oxides of interest here are nitric oxide (NO) and nitrogen dioxide (NO_2), the mixture of which is commonly referred to as "NO_x." While NO is clearly a precursor of photochemical oxidant, NO_2 is considered to be both an oxidant and a precursor of oxidants. Because of this "precursor" nature of NO_2 and the similarity of the analytical methods for NO and NO_2, the information on ambient NO_2 concentrations is presented in this chapter, dealing with the oxidant precursors, rather than in Chapter 2, which dealt with oxidants.

Analytical Methods

In air monitoring practices thus far, both NO and NO_2 have been measured colorimetrically, the NO requiring an intermediate step of oxidation into NO_2. Because of uncertainties and the somewhat controversial nature of the analytical methods for NO_x, these methods are discussed here in some detail.

The colorimetric Griess-Saltzman method is the most suitable manual method generally applicable to the measurement of NO_2 in the atmosphere.[12,13] The method can be used to determine concentrations of NO_2 in the air from 40 to 1500 mg/m^3 (0.02 to 0.80 ppm). Ordinarily, interferences are not a serious problem, although high ratios of sulfur dioxide to nitrogen dioxide (about 30:1) can cause bleaching

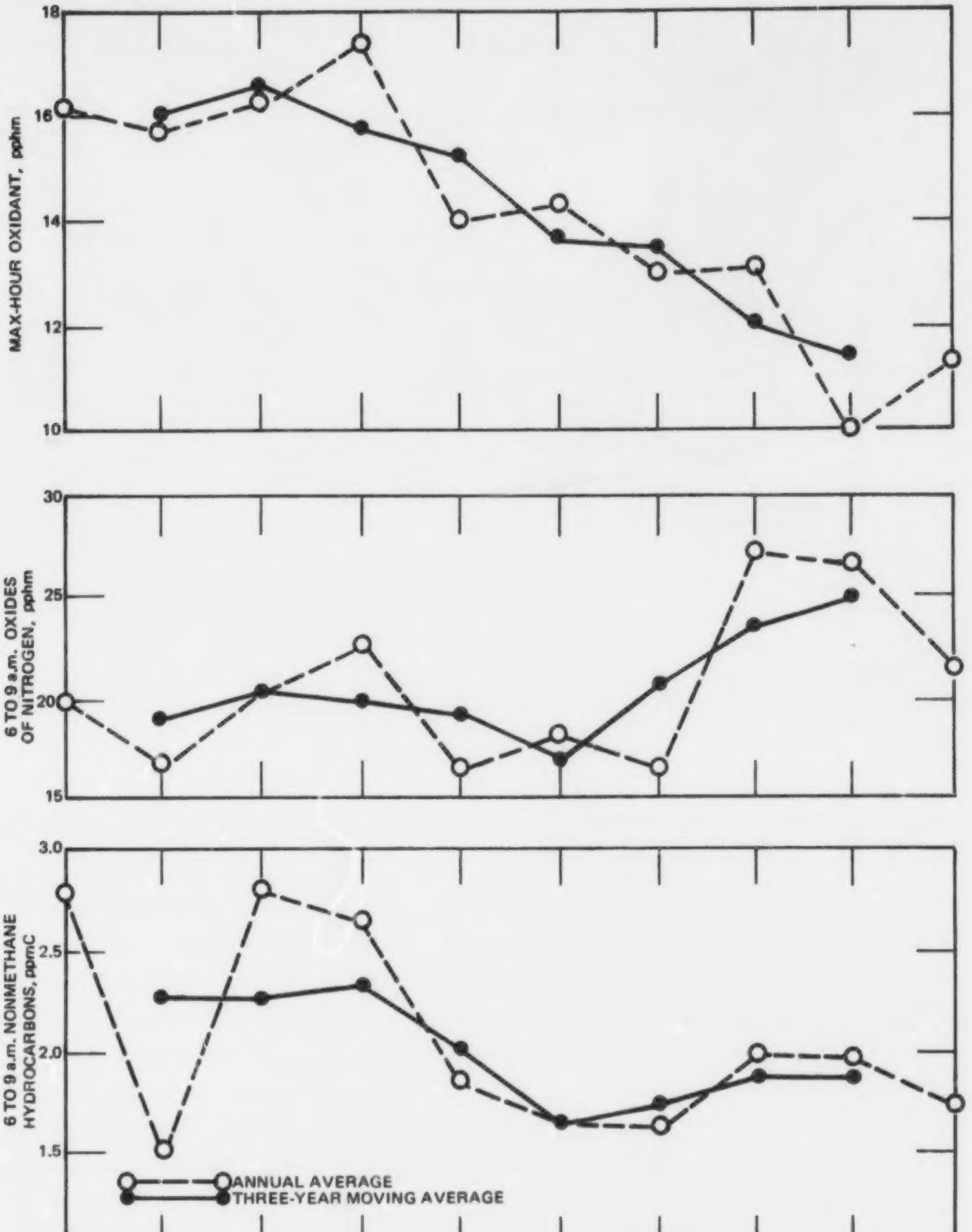

Figure 6-5. Pollutant trends for July, August, and September in Los Angeles, 1963-1972.[11]

and give misleadingly low values.[12] Interference from other oxides of nitrogen are negligible at concentrations found in polluted air. Peroxyacetyl nitrate (PAN) can give a response of up to 35 percent of an equivalent molar concentration of NO_2, but in ordinary ambient air, PAN concentrations are too low to cause sig-

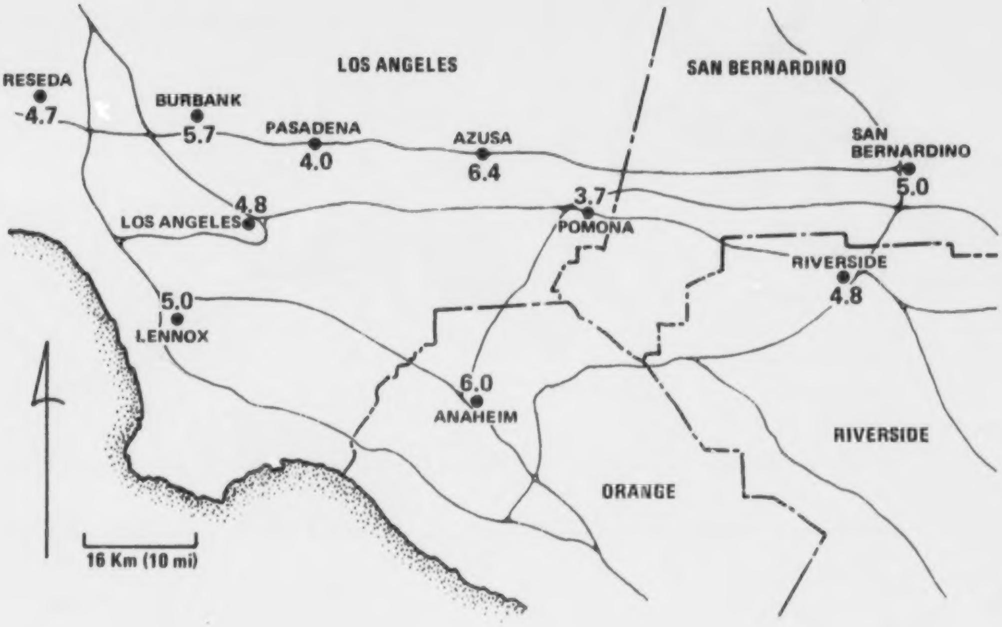

Figure 6-6. Distribution of total hydrocarbon concentrations in the South Coast Air Basin.[11] Average of daily maximum 1-hour concentrations (ppm C) during July, August, and September, 1970-1972.

nificant error.[12] More recent data suggest that ozone also, at high ozone to NO_2 ratios, may cause a negative inteference.[14]

In the original method, Saltzman[15] used solutions of sodium nitrite as calibration standards. He reported that, under laboratory conditions, 0.72 mole of nitrite produces the same color as 1 mole of NO_2 gas and incorporated this factor into his calculations. In recent years, this stoichiometric factor has been the source of considerable controversy. Values ranging from 0.5 to 1.00 have been reported,[16-22] and one recent study[23] reconfirmed Saltzman's original findings. The method can be standardized by using an accurately determined concentration of NO_2 gas, thus eliminating the stoichiometric factor from the calculations.

The NO is generally determined by oxidizing it to NO_2, measuring the resultant NO_2, and converting measurement results to NO concentrations. For the NO oxidation step, the oxidizers used are aqueous[24] or solid[25] potassium permangenate and dichromate or chromium trioxide in various formulations,[26-28] all of which have somewhat uncertain lifetimes at peak efficiency. In addition, the dichromate and chromium trioxide preparations are extremely sensitive to high humidity. More recently developed promising methods are the ones by Hartkamp[29] and by Forwerg and Creselius.[30]

It is generally believed that ambient NO concentrations are underestimated as a result of the poor conversion efficiency, a factor that should be kept in mind when studying NO data. Additional error may also be introduced depending on whether the NO measurement is done in series or in parallel with the NO_2 measurement, as explained next.

In the series mode, which some workers prefer, the sample air passes through an NO_2 analyzer for removal and measurement of NO_2, then through an oxidizer where NO is converted to NO_2, and finally through a second NO_2 analyzer.[31,32] The response from the second NO_2 analyzer is a measure of the NO in the sample air. However, up to 14 percent of the NO_2 may be converted to NO in the first analyzer. Therefore, it is better to remove the NO_2 by a special absorber, such as triethanolamine on firebrick.[33] Even in this case, up to a few percent of the NO_2 may be converted to NO depending on the humidity and the age of the absorber.

The parallel mode requires two separate analyses: in one, sample air is analyzed for NO_2; and in another, sample air is analyzed for total NO_x. In the latter analysis, the sample is passed through an oxidizing scrubber to convert NO to NO_2. Problems here are the uncertain efficiency of the scrubber as well as some retention of NO_2 in the scrubber.

The Griess-Saltzman method for NO_2 measurement cannot be used successfully when the delay between sample collection and color measurement is more than 4 to 6 hours or when sampling periods of longer than 1 hour are required. In such situations, the Jacobs-Hochheiser method has been preferred. With this method, sampling periods can be as long as 24 hours, and samples can be collected in the field and analyzed in a control laboratory with a delay of 2 weeks or more, if necessary. The method, however, has been found recently to have some serious drawbacks. New, soon to be published, studies have shown the Jacobs-Hochheiser method to suffer from NO_2 collection efficiency problems that cause erroneously high results for low NO_2 levels and low results for high NO_2 levels. Also, the method suffers from error due to positive interference from NO. Considerable improvement of the NO_2 collection efficiency was achieved by adding small amounts of sodium arsenite to the Jacobs-Hochheiser collection reagent.

Other recent developments have resulted in considerably improved methods for NO_x measurement. For example, use of permeation tubes now permits much more reliable calibration of the NO_2 measurement methods.[34] Also, new, highly promising, chemiluminescence methods have been developed for measurement of NO, and, indirectly, of NO_2 also.[29,35,36] Introduction of these new methods into U.S. monitoring networks was scheduled for completion by the end of 1974.

Concentrations

The majority of available continuous air quality data for nitrogen oxides are less than 15 years old. In 1956, the Los Angeles County Air Pollution Control

District (LAAPCD) began monitoring NO and NO_2 continuously. In 1961, the California State Department of Public Health organized the Statewide Cooperative Air Monitoring Network (SCAN), which, since 1968, has been operating 27 monitoring stations in California. Data on ambient NO_x have been obtained also by the Federal government through its Continuous Air Monitoring Program (CAMP) and the National Air Surveillance Networks (NASN). The data obtained in the SCAN and CAMP stations were by the continuous Griess-Saltzman method; NASN used the integrated Jacobs-Hochheiser method. These two analytical methods do not agree well; therefore, the respective data should be compared and interpreted carefully.

Tables 6-8 and 6-9 show frequency distribution data for 6 to 9 a.m. concentrations of NO and NO_2 measured at the CAMP stations. Data for 1963-1967 from selected cities in the California SCAN and LAAPCD networks are given in Tables 6-10 and 6-11. Table 6-12 includes data from various cities, showing NO_2 levels by the Jacobs-Hochheiser method, by the "arsenite" version of the Jacobs-Hochheiser procedure, and by the recently developed chemiluminescence method.[37]

The data given in the Tables 6-10 and 6-11 should be analyzed with care. It should be noted, for example, that these data, as given, do not show seasonal and diurnal effects and therefore cannot be directly associated with the oxidant levels observed in the respective locations. Since the interest here is on the role of NO_x in the oxidant formation process, the most useful data are those for NO_x from 6 to 9 a.m., because these data represent the NO_x concentrations that are assumed to cause the oxidant formed later in the day. Also, more pertinent data are those for NO_x concentrations during the summer and the early fall months when the oxidant levels are highest. In view of the large seasonal and diurnal variations in NO_x (see next section), a more appropriate compilation of ambient NO_x concentration data would emphasize data for 6 to 9 a.m. and for summer and early fall.

Seasonal and Diurnal Variations

Seasonal variation of ambient NO_x is illustrated in Figure 6-7, where frequency distribution data were plotted separately for each of the four seasons in 1964. The plots show the lowest NO_x levels to occur during the summer months and the highest during winter. Such variation is probably caused by increased accumulation of NO_x during the winter months, when early-morning temperature inversions (resulting in air stagnation) are more intense, and NO_x emissions from power generation and heating sources are increased.

Nitric oxide displays a more marked seasonal variation than NO_2 does. This can be seen when Figures 6-8 and 6-9 are compared.[38] For NO, as for most primary contaminants, higher mean values are observed during late fall and through the winter months, when there is less overall atmospheric mixing and generally less ultraviolet energy available for forming secondary products. The

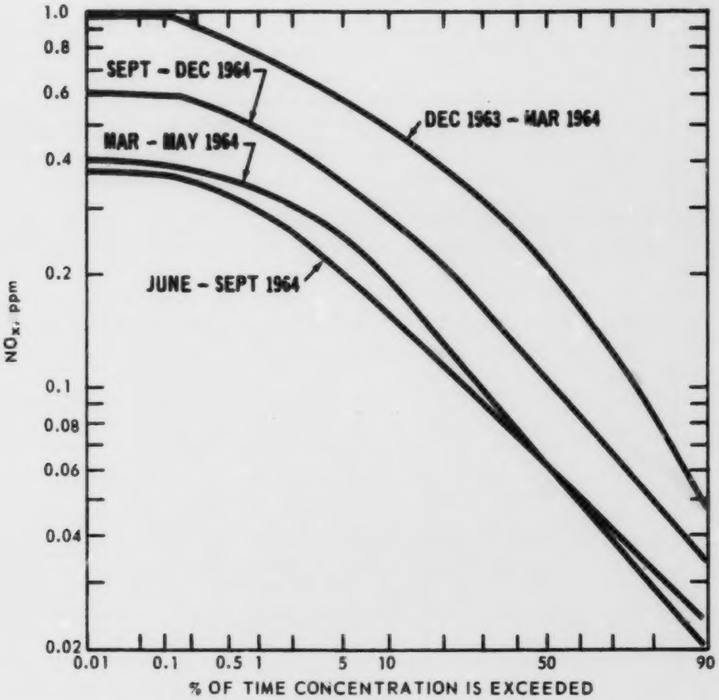

Figure 6-7. Frequency distribution of 3-hour-average concentrations of nitrogen oxides at Los Angeles CAMP Station, December 1, 1963, to December 1, 1964.

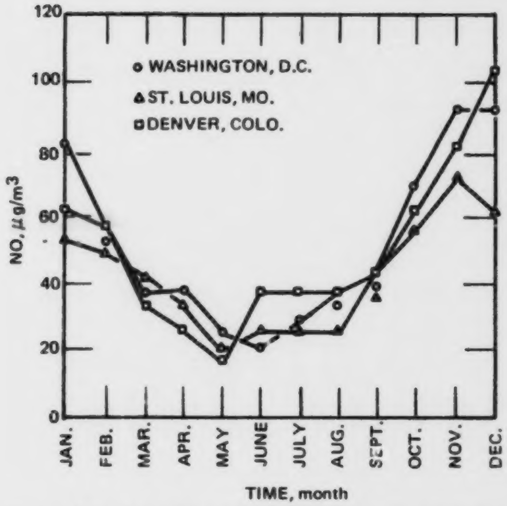

Figure 6-8. Monthly average of nitric oxide concentrations in three cities, 1969-1972.[38]

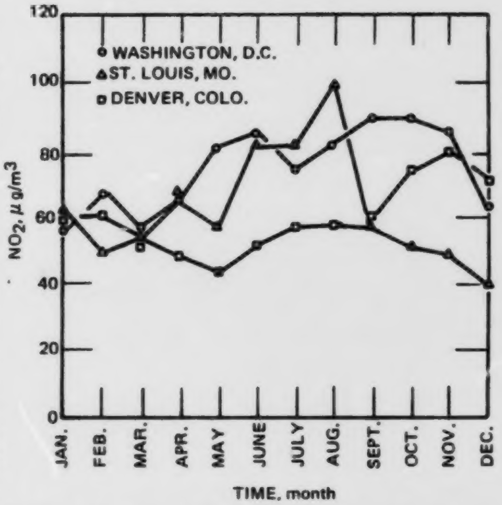

Figure 6-9. Monthly average of nitrogen dioxide concentrations in three cities, 1969-1972.[38]

pattern for NO_2 (Figure 6-9) is less distinct and shows less variation from month to month.

The diurnal variations of NO and NO_2 in Los Angeles, California, on July 19, 1965, are shown in Figure 6-10 along with the variations of carbon monoxide (CO)

Table 6-8. FREQUENCY DISTRIBUTION DATA FOR 6 TO 9 a.m. NITRIC OXIDE CONCENTRATIONS AT CAMP SITES, 1962-1972

Site	Year	Number of samples	Min.	Percentile[a]									Max.	Arithmetic		Geometric	
				10	20	30	40	50	60	70	80	90		Mean	Standard deviation	Mean	Standard deviation
San Francisco, California (056860002A10)	62[b]	112	0.00	0.00	0.00	0.01	0.01	0.02	0.02	0.03	0.04	0.06	0.13	0.02	0.02	0.02	2.51
	63[b]	179	0.00	0.00	0.00	0.01	0.02	0.02	0.03	0.05	0.06	0.08	0.32	0.03	0.03	0.02	2.98
	64[b]	13	0.01	0.01	0.02	0.02	0.03	0.04	0.04	0.05	0.06	0.20	0.29	0.07	0.08	0.04	2.63
Denver, Colorado (060580002A10)	65[b]	223	0.00	0.01	0.02	0.03	0.03	0.04	0.05	0.06	0.08	0.11	0.31	0.05	0.04	0.04	2.14
	66	297	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.11	0.15	0.30	0.07	0.06	0.05	2.61
	67[b]	191	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.09	0.13	0.32	0.06	0.05	0.05	2.31
	68[b]	192	0.00	0.01	0.02	0.02	0.04	0.05	0.06	0.07	0.10	0.14	0.27	0.06	0.05	0.04	2.71
	69	285	0.00	0.01	0.02	0.03	0.04	0.05	0.07	0.09	0.12	0.16	0.45	0.07	0.07	0.05	2.76
	70[b]	252	0.00	0.02	0.03	0.04	0.06	0.07	0.09	0.11	0.13	0.16	0.42	0.08	0.06	0.06	2.52
	71[b]	184	0.00	0.02	0.03	0.04	0.05	0.07	0.08	0.10	0.12	0.16	0.40	0.08	0.07	0.06	2.38
	72[b]	241	0.01	0.02	0.04	0.05	0.07	0.08	0.10	0.12	0.15	0.22	0.44	0.10	0.08	0.08	2.32
Washington, D.C. (090020002A10)	62	289	0.00	0.01	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.10	0.32	0.04	0.04	0.03	2.53
	63	279	0.00	0.00	0.01	0.02	0.02	0.04	0.05	0.06	0.08	0.13	0.40	0.06	0.06	0.04	2.82
	64	310	0.00	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.08	0.14	0.66	0.05	0.07	0.03	3.11
	65	274	0.00	0.00	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.12	0.38	0.05	0.06	0.03	2.83
	66	310	0.00	0.01	0.01	0.02	0.03	0.04	0.04	0.05	0.07	0.12	0.53	0.05	0.06	0.04	2.66
	67	304	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.10	0.16	0.74	0.07	0.08	0.05	2.74
	68[b]	270	0.00	0.01	0.02	0.03	0.03	0.04	0.05	0.06	0.08	0.13	0.49	0.06	0.06	0.04	2.56
Washington, D.C. (090020003A10)	69[b]	269	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.14	0.62	0.07	0.08	0.05	2.73
	70	299	0.00	0.01	0.02	0.03	0.04	0.06	0.07	0.09	0.11	0.16	0.54	0.08	0.08	0.05	2.80
	71	308	0.00	0.01	0.02	0.03	0.04	0.04	0.05	0.07	0.09	0.13	0.54	0.06	0.06	0.04	2.52
	72[b]	219	0.00	0.00	0.02	0.03	0.04	0.06	0.08	0.11	0.13	0.15	0.41	0.08	0.08	0.05	3.10
Chicago, Illinois (141220002A10)	62	283	0.00	0.04	0.05	0.07	0.09	0.11	0.13	0.16	0.19	0.21	0.56	0.12	0.08	0.10	2.14
	63	315	0.00	0.04	0.06	0.08	0.09	0.11	0.12	0.13	0.16	0.20	0.38	0.11	0.06	0.10	1.99
	64	318	0.00	0.04	0.06	0.07	0.09	0.11	0.13	0.15	0.17	0.24	0.71	0.13	0.09	0.10	2.06
	65	317	0.00	0.04	0.06	0.08	0.10	0.12	0.13	0.15	0.17	0.21	0.43	0.12	0.07	0.11	1.98
	66	286	0.00	0.04	0.07	0.09	0.11	0.13	0.15	0.17	0.19	0.23	0.51	0.13	0.08	0.12	1.99
	67	311	0.00	0.03	0.05	0.07	0.08	0.10	0.12	0.13	0.15	0.18	0.43	0.10	0.06	0.09	2.16
	68	319	0.00	0.03	0.04	0.06	0.07	0.09	0.10	0.12	0.15	0.19	0.37	0.10	0.06	0.08	2.13
	69	318	0.01	0.04	0.06	0.09	0.10	0.13	0.15	0.18	0.21	0.26	1.02	0.15	0.11	0.12	2.08
	70	320	0.00	0.04	0.08	0.10	0.13	0.15	0.19	0.24	0.28	0.33	0.65	0.18	0.11	0.14	2.31
	71[b]	263	0.00	0.04	0.07	0.09	0.11	0.13	0.16	0.20	0.22	0.27	0.51	0.15	0.09	0.12	2.08
	72	321	0.01	0.04	0.07	0.10	0.13	0.15	0.18	0.21	0.24	0.29	0.53	0.16	0.09	0.13	2.10

Table 6-8 (continued). FREQUENCY DISTRIBUTION DATA FOR 6 TO 9 a.m. NITRIC OXIDE CONCENTRATIONS AT CAMP SITES, 1962-1972

Site	Year	Number of samples	Min.	Percentile[a]									Max.	Arithmetic		Geometric	
				10	20	30	40	50	60	70	80	90		Mean	Standard deviation	Mean	Standard deviation
New Orleans, Louisiana (192020004A10)	62[b]	259	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.07	0.09	0.13	0.36	0.06	0.05	0.04	2.77
	63	325	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.24	0.02	0.02	0.02	2.45
St. Louis, Missouri (264280002A10)	64[b]	259	0.00	0.01	0.02	0.04	0.04	0.06	0.07	0.08	0.09	0.12	0.44	0.06	0.04	0.05	2.22
	65	333	0.00	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.19	0.04	0.03	0.03	2.70
	66	294	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.12	0.49	0.05	0.05	0.04	2.90
	67	326	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.07	0.08	0.11	0.26	0.05	0.04	0.04	2.58
	68[b]	256	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.11	0.28	0.05	0.04	0.04	2.80
	69	322	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.07	0.09	0.12	0.51	0.05	0.06	0.03	3.10
	70[b]	228	0.00	0.01	0.02	0.02	0.04	0.06	0.08	0.11	0.14	0.17	0.47	0.08	0.07	0.05	2.92
	71	311	0.00	0.01	0.02	0.03	0.05	0.06	0.08	0.10	0.12	0.15	0.36	0.07	0.06	0.06	2.47
	72[b]	234	0.00	0.01	0.02	0.03	0.05	0.07	0.10	0.12	0.14	0.19	0.40	0.09	0.07	0.06	2.48
Cincinnati, Ohio (361220003A10)	62	286	0.00	0.01	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.12	0.42	0.05	0.05	0.03	2.74
	63[b]	273	0.00	0.01	0.01	0.02	0.02	0.03	0.04	0.05	0.08	0.12	0.26	0.05	0.04	0.03	2.52
	64	334	0.00	0.01	0.01	0.01	0.02	0.03	0.04	0.05	0.09	0.13	0.45	0.05	0.07	0.03	2.90
	65	310	0.00	0.00	0.01	0.01	0.02	0.02	0.03	0.05	0.07	0.11	0.43	0.04	0.05	0.03	2.86
	66[b]	206	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.06	0.09	0.14	0.67	0.06	0.07	0.04	2.73
	67[b]	188	0.00	0.01	0.02	0.02	0.02	0.03	0.04	0.05	0.08	0.13	0.53	0.06	0.08	0.04	2.62
	68[b]	136	0.00	0.01	0.03	0.04	0.05	0.07	0.10	0.14	0.18	0.29	0.69	0.12	0.14	0.07	3.03
	69[b]	196	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.07	0.10	0.18	0.56	0.07	0.09	0.04	3.04
	70[b]	129	0.00	0.00	0.01	0.02	0.03	0.03	0.04	0.05	0.08	0.13	0.52	0.05	0.07	0.03	2.96
	71[b]	215	0.00	0.01	0.02	0.03	0.03	0.04	0.05	0.07	0.10	0.20	0.48	0.07	0.07	0.05	2.64
	72[b]	251	0.00	0.01	0.02	0.02	0.03	0.04	0.05	0.07	0.09	0.17	0.47	0.06	0.07	0.04	2.64
Philadelphia, Pennsylvania (397140002A10)	62[b]	239	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.03	0.06	0.23	0.02	0.02	0.02	2.54
	63[b]	233	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.07	0.10	0.15	0.79	0.07	0.10	0.04	3.30
	64	302	0.00	0.01	0.02	0.03	0.03	0.04	0.06	0.07	0.10	0.14	0.42	0.06	0.06	0.05	2.61
	65	290	0.00	0.01	0.02	0.02	0.04	0.04	0.06	0.07	0.10	0.16	0.64	0.07	0.07	0.05	2.65
	66	336	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.10	0.16	0.79	0.07	0.08	0.05	2.50
	67	296	0.00	0.02	0.03	0.04	0.05	0.07	0.08	0.10	0.13	0.17	0.71	0.09	0.08	0.07	2.38
	68[b]	266	0.00	0.01	0.02	0.03	0.04	0.05	0.07	0.08	0.12	0.17	0.55	0.08	0.08	0.05	2.60
	69	276	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.09	0.12	0.38	0.06	0.05	0.05	2.48
	70	305	0.00	0.01	0.03	0.04	0.05	0.06	0.08	0.10	0.12	0.16	0.81	0.08	0.09	0.06	2.47
	71	278	0.00	0.01	0.02	0.02	0.03	0.04	0.05	0.07	0.09	0.13	0.42	0.06	0.06	0.04	2.78

[a] Concentrations greater than or equal to specified value in indicated percentage of samples.

[b] Yearly standard exceeded.

Table 6-9. FREQUENCY DISTRIBUTION DATA FOR 6 TO 9 a.m. NITROGEN DIOXIDE CONCENTRATIONS AT CAMP SITES, 1962-1972

Site	Year	Number of samples	Min.	Percentile[a] 10	20	30	40	50	60	70	80	90	Max.	Arithmetic Mean	Arithmetic Standard deviation	Geometric Mean	Geometric Standard deviation
San Francisco, California (056860002A10)	62[b]	142	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.03	0.04	0.09	0.02	0.0.	0.02	2.23
	63[b]	155	0.00	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.04	0.06	0.19	0.03	0.02	0.03	1.80
	64[b]	10	0.01	0.01	0.02	0.03	0.04	0.04	0.04	0.04	0.05	0.05	0.06	0.04	0.01	0.04	1.54
Denver, Colorado (060580002A10)	65[b]	247	0.01	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.09	0.04	0.01	0.04	1.49
	66	324	0.00	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.10	0.04	0.01	0.04	1.47
	67[b]	180	0.00	0.02	0.02	0.03	0.03	0.04	0.04	0.04	0.05	0.06	0.09	0.04	0.01	0.04	1.57
	68[b]	226	0.00	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.11	0.04	0.01	0.04	1.64
	69	283	0.00	0.01	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.05	0.15	0.03	0.01	0.03	1.63
	70	282	0.00	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.07	0.13	0.04	0.02	0.04	1.76
	71[b]	171	0.00	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.06	0.10	0.03	0.01	0.03	1.66
	72[b]	253	0.00	0.01	0.02	0.03	0.03	0.04	0.04	0.05	0.06	0.07	0.12	0.04	0.02	0.04	1.78
Washington, D.C. (090020002A10)	62	313	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.05	0.16	0.03	0.01	0.03	1.76
	63	312	0.00	0.01	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.06	0.13	0.03	0.02	0.03	1.75
	64	308	0.01	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.06	0.15	0.03	0.01	0.04	1.63
	65	336	0.00	0.02	0.02	0.03	0.03	0.03	0.03	0.04	0.05	0.05	0.18	0.03	0.01	0.03	1.55
	66	275	0.00	0.02	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.13	0.03	0.01	0.03	1.61
	67	305	0.00	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.14	0.04	0.02	0.04	1.65
	68[b]	237	0.00	0.02	0.03	0.03	0.04	0.04	0.05	0.06	0.06	0.08	0.18	0.05	0.02	0.05	1.56
Washington, D.C. (090020003A10)	69[b]	254	0.00	0.02	0.02	0.03	0.03	0.04	0.04	0.04	0.05	0.06	0.11	0.04	0.01	0.04	1.56
	70	298	0.00	0.02	0.03	0.04	0.04	0.05	0.06	0.06	0.07	0.09	0.16	0.05	0.02	0.05	1.84
	71	318	0.01	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.11	0.03	0.01	0.04	1.50
	72[b]	214	0.00	0.00	0.02	0.03	0.03	0.04	0.04	0.05	0.06	0.09	0.40	0.05	0.06	0.04	2.55
Chicago, Illinois (141220002A10)	62	293	0.00	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.07	0.15	0.04	0.02	0.04	1.77
	63	318	0.00	0.02	0.03	0.03	0.03	0.03	0.04	0.04	0.05	0.06	0.11	0.04	0.01	0.04	1.49
	64	303	0.00	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.06	0.07	0.16	0.04	0.02	0.04	1.57
	65	330	0.01	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.06	0.11	0.04	0.01	0.04	1.43
	66	304	0.00	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.07	0.09	0.23	0.05	0.02	0.05	1.56
	67	290	0.00	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.07	0.17	0.04	0.02	0.04	1.62
	68	312	0.01	0.03	0.03	0.03	0.04	0.04	0.05	0.05	0.05	0.06	0.10	0.04	0.01	0.04	1.45
	69	330	0.00	0.03	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.07	0.17	0.04	0.02	0.05	1.51
	70	329	0.00	0.03	0.04	0.04	0.04	0.05	0.05	0.06	0.07	0.08	0.14	0.05	0.02	0.05	1.50
	71	285	0.02	0.03	0.03	0.04	0.04	0.04	0.05	0.06	0.07	0.08	0.39	0.06	0.05	0.05	1.67
	72	336	0.00	0.03	0.03	0.04	0.04	0.04	0.05	0.06	0.06	0.08	0.16	0.05	0.02	0.05	1.60

Table 6-9 (continued). FREQUENCY DISTRIBUTION DATA FOR 6 TO 9 a.m. NITROGEN DIOXIDE CONCENTRATIONS AT CAMP SITES, 1962-1972

Site	Year	Number of samples	Percentile[a]										Max.	Arithmetic		Geometric	
			Min.	10	20	30	40	50	60	70	80	90		Mean	Standard deviation	Mean	Standard deviation
New Orleans, Louisiana (192020004A10)	62	288	0.00	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.07	0.14	0.04	0.02	0.04	1.79
	63	289	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.03	0.05	0.01	0.00	0.02	1.86
St. Louis, Missouri (264280002A10)	64[b]	255	0.00	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.06	0.16	0.03	0.02	0.03	1.85
	65	348	0.00	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.03	0.04	0.08	0.02	0.01	0.02	1.80
	66	322	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.04	0.04	0.06	0.12	0.03	0.01	0.03	1.80
	67	352	0.00	0.01	0.01	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.06	0.02	0.01	0.02	1.83
	68	322	0.00	0.00	0.01	0.01	0.02	0.02	0.02	0.02	0.03	0.04	0.11	0.02	0.01	0.02	1.94
	69[b]	258	0.00	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.04	0.05	0.11	0.02	0.01	0.02	2.11
	70[b]	233	0.00	0.01	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.05	0.10	0.02	0.01	0.03	1.66
	71	309	0.00	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.05	0.06	0.11	0.03	0.01	0.03	1.61
	72[b]	231	0.01	0.02	0.02	0.03	0.03	0.04	0.05	0.06	0.07	0.08	0.16	0.04	0.02	0.04	1.66
Cincinnati, Ohio (361220003A10)	62	292	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.05	0.13	0.03	0.01	0.03	1.82
	63	304	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.05	0.13	0.03	0.01	0.03	1.71
	64	336	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.06	0.15	0.03	0.01	0.03	1.77
	65	313	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.10	0.03	0.01	0.03	1.45
	66[b]	238	0.00	0.02	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.06	0.11	0.03	0.01	0.03	1.69
	67[b]	223	0.00	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.04	0.09	0.02	0.01	0.03	1.52
	68	280	0.00	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.09	0.03	0.01	0.03	1.59
	69[b]	231	0.00	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.05	0.10	0.03	0.01	0.03	1.56
	70[b]	129	0.01	0.02	0.03	0.03	0.03	0.03	0.04	0.04	0.05	0.07	0.12	0.04	0.02	0.04	1.53
	71[b]	236	0.00	0.01	0.02	0.02	0.02	0.03	0.04	0.04	0.05	0.07	0.11	0.03	0.02	0.03	2.00
	72[b]	227	0.00	0.02	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.06	0.13	0.04	0.01	0.04	1.64
Philadelphia, Pennsylvania (397140002A10)	62[b]	211	0.00	0.00	0.01	0.01	0.02	0.02	0.02	0.03	0.03	0.04	0.10	0.02	0.01	0.02	1.56
	63	286	0.00	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.07	0.15	0.03	0.02	0.03	1.97
	64	281	0.00	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.07	0.20	0.04	0.02	0.04	1.72
	65	286	0.00	0.02	0.0[illegible]	0.02	0.03	0.03	0.03	0.04	0.05	0.05	0.12	0.03	0.01	0.03	1.58
	66	340	0.00	0.02	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.06	0.11	0.03	0.01	0.03	1.66

[a] Concentrations greater than or equal to specified value in indicated percentage of samples.

[b] Yearly standard exceeded.

Table 6-10. NITRIC OXIDE CONCENTRATION[a] IN CALIFORNIA BY AVERAGING TIME AND FREQUENCY, 1963-1967
(ppm)

Place, site No., averaging time	Maximum for year					Percentile[b]							
	63	64	65	66	67	0.01	0.1	1	10	30	50	70	90
Anaheim-176													
1 hr	0.29	0.30	0.70	0.40	0.66	0.62	0.40	0.22	0.07	0.03	0.01	0.00	0.00
8 hr	0.18	0.19	0.29	0.24	0.41		0.28	0.18	0.07	0.03	0.02	0.01	0.00
1 day	0.11	0.09	0.17	0.15	0.18			0.12	0.06	0.03	0.02	0.01	0.00
1 mo	0.05	0.04	0.05	0.04	0.07				0.06	0.04	0.02	0.02	0.01
1 yr	0.02			0.02	0.04						0.02		
Bakersfield-201													
1 hr	0.34			0.44	0.56	0.55	0.40	0.25	0.09	0.03	0.01	0.00	0.00
8 hr	0.20			0.27	0.36		0.28	0.18	0.08	0.03	0.02	0.00	0.00
1 day	0.12			0.16	0.22			0.14	0.07	0.03	0.02	0.01	0.00
1 mo	0.05			0.07	0.09				0.06	0.04	0.02	0.02	0.01
1 yr				0.02	0.04						0.04		
Fresno-226													
1 hr	0.87	0.47	0.52	0.54	0.59	0.72	0.41	0.22	0.04	0.01	0.00	0.00	0.00
8 hr	0.49	0.22	0.25	0.24	0.30		0.26	0.16	0.04	0.01	0.00	0.00	0.00
1 day	0.21	0.15	0.14	0.12	0.14			0.11	0.04	0.01	0.00	0.00	0.00
1 mo	0.03	0.06	0.03	0.04	0.05				0.04	0.02	0.01	0.00	0.00
1 yr	0.01	0.02	0.02		0.02						0.02		
Oakland-327													
1 hr	0.93	0.93	0.66	0.68	0.91	0.92	0.70	0.41	0.15	0.05	0.02	0.01	0.00
8 hr	0.57	0.60	0.34	0.34	0.52		0.55	0.32	0.14	0.05	0.03	0.01	0.00
1 day	0.33	0.35	0.26	0.26	0.30			0.26	0.13	0.06	0.03	0.02	0.01
1 mo	0.02	0.14	0.11	0.13	0.11				0.11	0.07	0.04	0.02	0.02
1 yr		0.07	0.05	0.05	0.05						0.05		
Port Chicago-429													
1 hr				0.14	0.24	0.18	0.13	0.08	0.03	0.01	0.00	0.00	0.00
8 hr				0.07	0.12		0.10	0.06	0.03	0.01	0.01	0.00	0.00
1 day				0.06	0.07			0.05	0.02	0.01	0.01	0.00	0.00
1 mo				0.02	0.02				0.02	0.01	0.01	0.01	0.00
1 yr				0.01	0.01						0.01		
Richmond-428													
1 hr				0.74	0.58	0.74	0.49	0.27	0.10	0.04	0.02	0.01	0.00
8 hr				0.45	0.35		0.35	0.23	0.10	0.05	0.02	0.01	0.00
1 day				0.20	0.21			0.18	0.09	0.05	0.03	0.01	0.00
1 mo				0.07	0.08				0.08	0.07	0.04	0.02	0.01
1 yr					0.04						0.04		
Riverside-126													
1 hr		1.10	0.57	0.43	0.52	0.74	0.47	0.29	0.11	0.04	0.02	0.01	0.00
8 hr		0.59	0.36	0.26	0.26		0.38	0.21	0.10	0.04	0.02	0.01	0.00
1 day		0.28	0.24	0.20	0.20			0.18	0.09	0.05	0.03	0.01	0.00
1 mo		0.11	0.10	0.08	0.08				0.08	0.05	0.03	0.03	0.01
1 yr			0.04	0.04	0.04						0.04		
Sacramento-276													
1 hr	1.08	1.08	0.97	0.75	0.90	0.97	0.70	0.37	0.09	0.03	0.02	0.00	0.00
8 hr	0.60	0.53	0.62	0.49	0.58		0.54	0.29	0.09	0.03	0.02	0.01	0.00
1 day	0.35	0.26	0.28	0.23	0.33			0.22	0.09	0.04	0.02	0.01	0.00
1 mo	0.14	0.09	0.10	0.07	0.07				0.07	0.05	0.03	0.01	0.01
1 yr	0.04	0.04	0.03	0.04	0.03						0.04		

Table 6-10 (continued). NITRIC OXIDE CONCENTRATION[a] IN CALIFORNIA BY AVERAGING TIME AND FREQUENCY, 1963-1967 (ppm)

Place, site No., averaging time	Maximum for year					Percentile[b]							
	63	64	65	66	67	0.01	0.1	1	10	30	50	70	90
Salinas-536													
1 hr				0.45	0.29	0.45	0.24	0.15	0.05	0.01	0.00	0.00	0.00
8 hr				0.21	0.15		0.20	0.10	0.04	0.02	0.01	0.00	0.00
1 day				0.10	0.07			0.06	0.04	0.02	0.01	0.00	0.00
1 mo				0.04	0.03				0.03	0.02	0.01	0.01	0.00
1 yr					0.01						0.01		
San Bernardino-151													
1 hr	0.25	0.25	0.34	0.50	0.36	0.47	0.32	0.15	0.05	0.02	0.01	0.00	0.00
8 hr	0.12	0.12	0.16	0.26	0.15		0.25	0.12	0.05	0.02	0.01	0.01	0.00
1 day	0.06	0.06	0.10	0.20	0.11			0.09	0.05	0.03	0.02	0.01	0.00
1 mo	0.03	0.02	0.04	0.07	0.05				0.04	0.03	0.02	0.01	0.00
1 yr	0.01				0.03						0.03		
San Diego-101													
1 hr	0.74	1.10	0.90	1.20	0.80	1.00	0.65	0.38	0.10	0.02	0.01	0.00	0.00
8 hr	0.45	0.63	0.43	0.42	0.34		0.42	0.26	0.10	0.03	0.01	0.00	0.00
1 day	0.24	0.21	0.23	0.26	0.22			0.20	0.10	0.04	0.01	0.00	0.00
1 mo	0.14	0.08	0.09	0.12	0.10				0.09	0.05	0.02	0.01	0.00
1 yr	0.04	0.02	0.03	0.05	0.04						0.04		
San Diego-106													
1 hr		0.40	0.56	0.34		0.40	0.31	0.21	0.05	0.00	0.00	0.00	0.00
8 hr		0.26	0.22	0.15			0.22	0.13	0.06	0.01	0.00	0.00	0.00
1 day		0.12	0.12	0.08				0.10	0.05	0.02	0.00	0.00	0.00
1 mo		0.05	0.04						0.05	0.02	0.00	0.00	0.00
1 yr		0.02	0.01								0.02		
San Diego-108													
1 hr				0.52	0.60	0.60	0.40	0.20	0.07	0.03	0.01	0.00	0.00
8 hr				0.18	0.29		0.25	0.16	0.07	0.03	0.02	0.01	0.00
1 day				0.14	0.16			0.12	0.06	0.03	0.02	0.01	0.00
1 mo				0.07	0.08				0.05	0.03	0.02	0.02	0.00
1 yr				0.03	0.03						0.03		
San Jose-376													
1 hr	0.75	0.60	0.39	0.42	0.68	0.68	0.54	0.37	0.17	0.07	0.03	0.01	0.00
8 hr	0.48	0.46	0.22	0.25	0.38		0.46	0.29	0.15	0.08	0.04	0.02	0.01
1 day	0.26	0.27	0.17	0.15	0.21			0.25	0.15	0.08	0.04	0.02	0.01
1 mo	0.17	0.14	0.12		0.08				0.12	0.08	0.07	0.02	0.02
1 yr					0.04						0.04		
Santa Barbara-351													
1 hr		0.38	0.72	0.57		0.68	0.51	0.32	0.07	0.01	0.01	0.00	0.00
8 hr		0.19	0.45	0.29			0.40	0.22	0.07	0.02	0.01	0.00	0.00
1 day		0.10	0.21	0.18				0.18	0.08	0.02	0.01	0.00	0.00
1 mo		0.04	0.11	0.10					0.06	0.03	0.01	0.01	0.00
1 yr			0.03								0.03		
Stockton-252													
1 hr	0.38	0.50	0.48	0.87	0.36	0.68	0.47	0.27	0.08	0.02	0.01	0.00	0.00
8 hr	0.18	0.29	0.33	0.50	0.16		0.39	0.23	0.07	0.02	0.01	0.00	0.00
1 day	0.14	0.15	0.23	0.26	0.09			0.19	0.07	0.03	0.01	0.01	0.00
1 mo	0.04	0.06	0.11	0.11	0.02				0.06	0.03	0.02	0.01	0.00
1 yr		0.03	0.03	0.03	0.01						0.03		

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[a] Determined by continuous Griess-Saltzman method.

[b] Concentrations greater than or equal to specified value in indicated percentage of samples.

Table 6-11. NITROGEN DIOXIDE CONCENTRATION[a] IN CALIFORNIA BY AVERAGING TIME AND FREQUENCY, 1963-1967
(ppm)

Place, site No., averaging time	Maximum for year					Percentile[b]							
	63	64	65	66	67	0.01	0.1	1	10	30	50	70	90
Anaheim-176													
1 hr	0.20	0.22	0.23	0.27	0.27	0.25	0.21	0.15	0.07	0.05	0.03	0.02	0.01
8 hr	0.15	0.13	0.16	0.15	0.19		0.18	0.13	0.07	0.04	0.03	0.02	0.01
1 day	0.11	0.11	0.13	0.12	0.13			0.10	0.06	0.04	0.03	0.02	0.01
1 mo	0.06	0.04	0.05	0.05	0.07				0.06	0.05	0.04	0.03	0.02
1 yr	0.03			0.04	0.04						0.04		
Bakersfield-201													
1 hr	0.17			0.15	0.19	0.19	0.14	0.10	0.06	0.04	0.03	0.02	0.01
8 hr	0.10			0.10	0.14		0.13	0.09	0.06	0.04	0.03	0.02	0.01
1 day	0.07			0.08	0.09			0.08	0.05	0.04	0.03	0.03	0.02
1 mo	0.03			0.04	0.05				0.04	0.04	0.03	0.03	0.03
1 yr				0.03	0.04						0.04		
Fresno-226													
1 hr	0.10	0.17	0.25	0.14	0.17	0.22	0.14	0.09	0.04	0.03	0.02	0.01	0.01
8 hr	0.08	0.10	0.18	0.11	0.12		0.13	0.08	0.04	0.03	0.02	0.01	0.01
1 day	0.05	0.08	0.11	0.06	0.07			0.06	0.04	0.03	0.02	0.02	0.01
1 mo	0.03	0.04	0.04	0.04	0.05				0.03	0.03	0.02	0.02	0.02
1 yr	0.02	0.02	0.02	0.03	0.03						0.02		
Oakland-327													
1 hr	0.28	0.41	0.23	0.29	0.33	0.33	0.23	0.14	0.07	0.04	0.03	0.02	0.01
8 hr	0.19	0.25	0.15	0.18	0.23		0.20	0.13	0.06	0.04	0.03	0.02	0.01
1 day	0.10	0.16	0.10	0.13	0.15			0.10	0.06	0.04	0.03	0.02	0.02
1 mo	0.05	0.05	0.06	0.05	0.06				0.05	0.04	0.03	0.03	0.02
1 yr	0.03	0.03	0.03	0.03	0.04						0.03		
Port Chicago-429													
1 hr				0.17	0.14	0.15	0.11	0.08	0.04	0.03	0.02	0.02	0.01
8 hr				0.09	0.07		0.09	0.07	0.04	0.03	0.02	0.02	0.01
1 day				0.07	0.06			0.06	0.04	0.03	0.02	0.02	0.01
1 mo				0.03	0.04				0.03	0.03	0.03	0.02	0.02
1 yr				0.03	0.03						0.03		
Richmond-428													
1 hr				0.14	0.21	0.21	0.15	0.10	0.06	0.04	0.03	0.02	0.01
8 hr				0.08	0.14		0.10	0.08	0.06	0.04	0.03	0.02	0.01
1 day				0.07	0.10			0.07	0.05	0.04	0.03	0.02	0.02
1 mo				0.03	0.05				0.05	0.04	0.03	0.03	0.02
1 yr					0.03						0.03		
Riverside-126													
1 hr	0.27	0.56	0.49	0.25	0.31	0.49	0.32	0.18	0.09	0.05	0.03	0.02	0.01
8 hr	0.18	0.26	0.31	0.18	0.23		0.29	0.15	0.08	0.05	0.04	0.02	0.01
1 day	0.14	0.19	0.25	0.13	0.17			0.14	0.07	0.05	0.04	0.03	0.02
1 mo	0.06	0.05	0.08	0.05	0.05				0.05	0.05	0.04	0.04	0.03
1 yr		0.04	0.05	0.04	0.04						0.04		
Sacramento-276													
1 hr	0.29	0.32	0.30	0.27	0.30	0.30	0.22	0.14	0.07	0.04	0.03	0.02	0.01
8 hr	0.17	0.21	0.20	0.21	0.20		0.19	0.12	0.06	0.04	0.03	0.02	0.01
1 day	0.13	0.13	0.13	0.15	0.13			0.11	0.06	0.04	0.03	0.02	0.02
1 mo	0.07	0.07	0.07	0.05	0.05				0.05	0.04	0.03	0.03	0.02
1 yr	0.04	0.04	0.04	0.03	0.04						0.04		
Salinas-536													
1 hr				0.11	0.10	0.11	0.09	0.06	0.03	0.02	0.02	0.01	0.01
8 hr				0.07	0.08		0.07	0.05	0.03	0.02	0.02	0.01	0.01
1 day				0.05	0.05			0.04	0.03	0.02	0.02	0.01	0.01
1 mo				0.03	0.02				0.02	0.02	0.02	0.02	0.01
1 yr					0.02						0.02		

Table 6-11 (continued). NITROGEN DIOXIDE CONCENTRATION[a] IN CALIFORNIA BY AVERAGING TIME AND FREQUENCY, 1963-1967 (ppm)

Place, site No., averaging time	Maximum for year					Percentile[b]							
	63	64	65	66	67	0.01	0.1	1	10	30	50	70	90
San Bernadino-151													
1 hr	0.14	0.06	0.11	0.25	0.22	0.23	0.19	0.13	0.07	0.04	0.02	0.01	0.00
8 hr	0.12	0.03	0.07	0.14	0.17		0.16	0.12	0.06	0.04	0.02	0.01	0.00
1 day	0.06	0.02	0.05	0.11	0.13			0.10	0.06	0.04	0.03	0.01	0.00
1 mo	0.03		0.03	0.06	0.07				0.05	0.04	0.03	0.01	0.00
1 yr	0.01			0.04	0.05						0.04		
San Diego-101													
1 hr	0.33	0.35	0.52	0.40	0.34	0.35	0.22	0.12	0.06	0.03	0.01	0.00	0.00
8 hr	0.18	0.15	0.22	0.19	0.17		0.18	0.11	0.06	0.03	0.02	0.01	0.00
1 day	0.12	0.09	0.12	0.12	0.08			0.09	0.05	0.03	0.02	0.01	0.00
1 mo	0.06	0.06	0.04	0.06	0.03				0.04	0.03	0.02	0.01	0.01
1 yr	0.03	0.02	0.02	0.03	0.02						0.02		
San Diego-106													
1 hr		0.20	0.17	0.15		0.17	0.14	0.10	0.04	0.01	0.00	0.00	0.00
8 hr		0.11	0.09	0.11			0.11	0.09	0.04	0.01	0.00	0.00	0.00
1 day		0.09	0.05	0.07				0.07	0.03	0.01	0.00	0.00	0.00
1 mo		0.05	0.02						0.02	0.02	0.01	0.00	0.00
1 yr		0.01	0.01								0.01		
San Diego-108													
1 hr				0.37	0.21	0.35	0.25	0.13	0.06	0.03	0.02	0.01	0.00
8 hr				0.25	0.13		0.18	0.12	0.15	0.03	0.02	0.01	0.00
1 day				0.14	0.08			0.10	0.05	0.03	0.02	0.02	0.01
1 mo				0.06	0.04				0.05	0.03	0.02	0.02	0.01
1 yr				0.03	0.02						0.03		
San Jose-376													
1 hr	0.30	0.39	0.23	0.27	0.27	0.34	0.29	0.18	0.09	0.05	0.04	0.03	0.01
8 hr	0.19	0.31	0.16	0.20	0.18		0.24	0.16	0.09	0.05	0.04	0.03	0.02
1 day	0.13	0.18	0.12	0.16	0.12			0.13	0.08	0.05	0.04	0.03	0.02
1 mo	0.07	0.07	0.07	0.06	0.07				0.07	0.05	0.04	0.04	0.03
1 yr		0.05		0.04	0.04						0.04		
Santa Barbara-351													
1 hr		0.18	0.31	0.13		0.28	0.14	0.08	0.05	0.03	0.02	0.02	0.01
8 hr		0.12	0.13	0.08			0.12	0.07	0.05	0.03	0.02	0.02	0.01
1 day		0.09	0.08	0.06				0.07	0.04	0.03	0.02	0.02	0.01
1 mo		0.03	0.04	0.03					0.03	0.03	0.03	0.02	0.02
1 yr		0.02	0.03								0.03		
Santa Cruz-841													
1 hr			0.12	0.09		0.12	0.08	0.06	0.03	0.02	0.01	0.01	0.01
8 hr				0.07	0.06		0.06	0.05	0.03	0.02	0.02	0.01	0.01
1 day				0.04	0.04			0.04	0.03	0.02	0.02	0.01	0.01
1 mo				0.02	0.02				0.02	0.02	0.02	0.02	0.01
1 yr					0.02						0.02		
Stockton-252													
1 hr	0.13	0.22	0.14	0.16	0.18	0.20	0.16	0.09	0.04	0.02	0.02	0.01	0.01
8 hr	0.08	0.15	0.11	0.11	0.10		0.12	0.07	0.04	0.03	0.02	0.01	0.01
1 day	0.06	0.08	0.07	0.07	0.06			0.06	0.04	0.03	0.02	0.02	0.01
1 mo	0.02	0.05	0.03	0.03	0.03				0.03	0.02	0.02	0.02	0.01
1 yr		0.03	0.02	0.02	0.02						0.02		

[a] Determined by continuous Griess-Saltzman method.

[b] Concentrations greater than or equal to specified value in indicated percentage of samples.

Table 6-12. AMBIENT NITROGEN DIOXIDE CONCENTRATIONS IN VARIOUS CITIES IN 1972 MEASURED BY DIFFERENT METHODS (arithmetic average for period of operation)

City	NO_2 concentration, $\mu g/m^3$		
	Jacobs-Hochheiser	Arsenite	Chemiluminescence
Los Angeles, Cal.	252	182	118
Chicago, Ill.[a]	238	117	121
Salt Lake City, Utah	159	62	114
Denver, Colo.[a]	106	42	110
New York-New Jersey	182	100	65
Baltimore, Md.	159	96	64
Washington, D.C.[a]	146	88	64
San Jose, Cal.[a]	193	85	84
Louisville, Ky.	184	87	68
Springfield, Mass.	125	82	73
Phoenix, Ariz.	159	80	69
Atlanta, Ga.	183	80	62
Detroit, Mich.	180	80	60
St. Louis, Mo.[a]	123	79	58
Pittsburgh, Pa.	177	78	64
Dallas, Texas	145	76	47
Columbus, Ohio	149	68	52
Memphis, Tenn.	148	64	31
Houston, Texas	137	64	66
San Diego, Cal.	136	63	76
Dayton, Ohio	158	64	53
Indianapolis, Ind.	107	61	56
Omaha, Neb.	113	60	30
Lancaster, Pa.	132	60	36
Grand Rapids, Mich.	127	59	44
Richmond, Va.	171	58	37
Canton, Ohio	126	57	53
Miami, Fla.	120	55	53
Tampa, Fla.	156	56	52
Toledo, Ohio	139	54	38
Reading, Pa.	158	52	60
Rochester, N. Y.	98	48	26
Seattle, Wash.	134	47	51
Providence, R. I.	98	45	--
Philadelphia, Pa.	197	83	84
Corpus Christi, Texas	85	43	43
Cincinnati, Ohio	156	73	61
Buffalo, N. Y.	76	32	49
Dubuque, Iowa	70	30	23
Worcester, Mass.	120	71	--
Chattanooga, Tenn.	125	53	38
Boston, Mass.	132	74	--
Milwaukee, Wis.	124	76	--
Johnstown, Pa.	--	25	64

[a] Common site for all instruments.

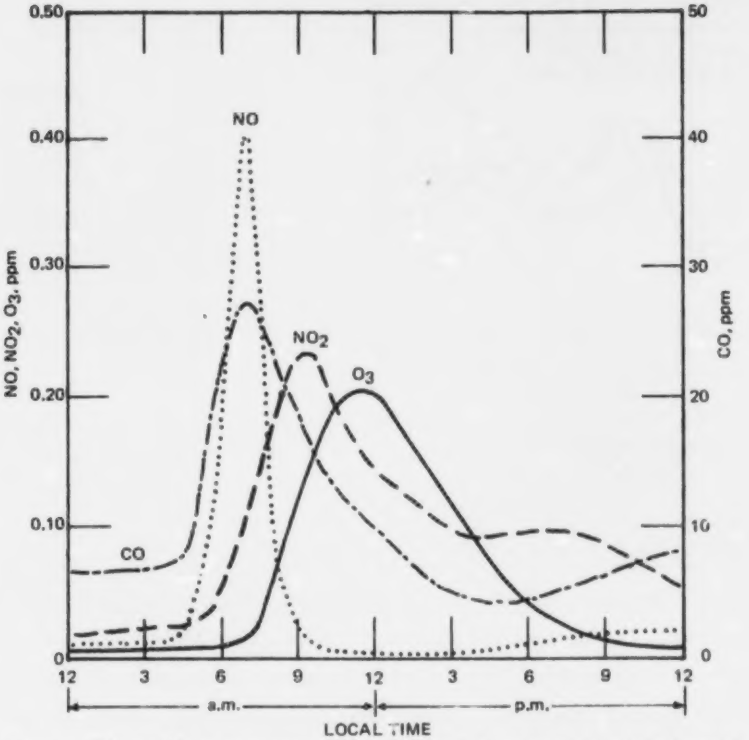

Figure 6-10. Average daily 1-hour concentrations of selected pollutants in Los Angeles, California, July 19, 1965.[39]

and ozone (O_3).[39] This concentration profile graphically depicts the NO peak and the associated lag in NO_2 peak as the NO is converted. It also illustrates the subsequent increase in O_3 concentration. The data in Figure 6-10 do not show the generalized increase in evening NO_x levels due to the late afternoon peak automotive traffic. On this particular day, evening dispersion factors apparently prevented any substantial buildup of the NO_x. It should be pointed out that Los Angeles, however, is a unique city because of the tremendous influence of automobile emissions; other cities would not necessarily exhibit the same characteristics. Figure 6-11 shows diurnal variations in NO_2 concentration in several other cities.[38]

The hours at which the peak concentrations of NO_x usually occur either coincide with, or take place shortly after, the hours of peak automotive traffic. The diurnal pattern, therefore, shows little day-to-day variation except for weekends and holidays, when traffic differs from weekday patterns. The diurnal variations of NO on weekdays, Saturdays, and Sundays are shown for the Chicago CAMP station in Figure 6-12.[40] The Sunday peak concentrations of NO at 8 a.m. are about one-third of the weekday peak concentrations. On some weekends, some locations have peak NO concentrations equal to weekday peak values, but the peaks occur 1 to 3 hours later. Furthermore, weekend NO concentrations in certain recreational areas often exceed weekday values.

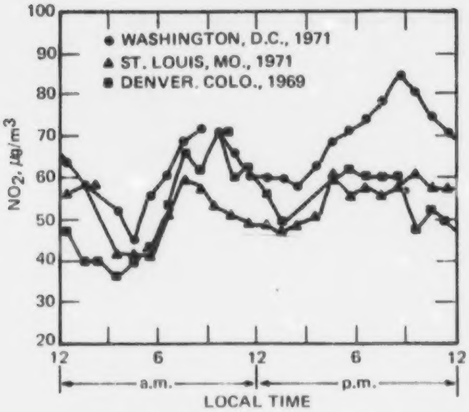

Figure 6-11. Diurnal variation of nitrogen dioxide concentrations at sites in the United States.[38]

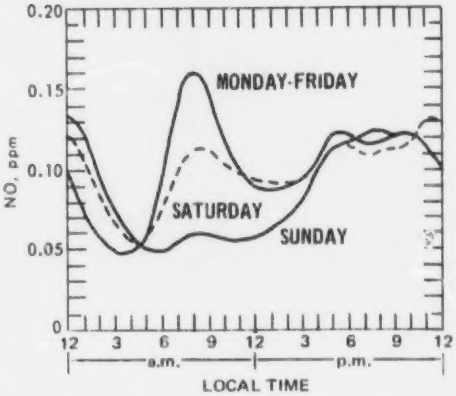

Figure 6-12. Weekday and weekend 1-hour-average nitric oxide levels in Chicago, Illinois, 1962-1964.[40]

Nitrogen Oxide Trends

As with the oxidant and hydrocarbon trends, the NO_x trends discussed here are those observed in the Los Angeles air basin, for which the atmospheric data available are abundant.[11] Such data consist of NO and NO_2 measurements by the Saltzman method and were taken from 14 monitoring stations operated during most of the period 1963-1972. The data are presented in Tables 6-13 through 6-18, using the following presentation forms:

1. The average of maximum hourly concentrations during July, August, and September (an average of 92 values per year).
2. The average concentrations from 6 to 9 a.m. during July, August, and September (an average of 276 one-hour values each year).
3. The annual average of maximum hourly concentrations (an average of 365 values each year).

Trends of NO_x in Los Angeles are depicted graphically in Figure 6-13. Corresponding trends of oxidant, nonmethane hydrocarbon, and NO_x are shown in Figure 6-5. Figures 6-14 and 6-15 show distributions of NO_x and NO_2, respectively, in the Los Angeles air basin. It is interesting to note that the locations in the Los Angeles basin with the highest NO_x, NO_2, and hydrocarbon concentrations are not the locations with the highest oxidant concentrations. The data in Table 6-19, taken from Figures 2-9, 6-6, 6-14, and 6-15, illustrate this point. The Los Angeles station had NO_x and NO_2 values above the basinwide averages, hydrocarbon values about the same as the basinwide average, and oxidant values below the basinwide average. On the other hand, Azusa and San Bernardino had NO_x and NO_2 values below the basinwide average, hydrocarbons equal to or above the basinwide average, and oxidant values above the basinwide average. Anaheim had lower NO_x, NO_2, and oxidant and higher hydrocarbon values relative

Table 6-13. OXIDES OF NITROGEN TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF DAILY MAXIMUM ONE-HOUR CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a,11]
(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	6.0	7.4	7.2	14.8	13.2	18.3	16.7	12.9	17.5	14.6
Azusa	10.7	12.9	10.8	12.4	13.0	13.6	13.4	19.3	19.0	16.2
Burbank	17.3	18.0	23.6	20.7	22.6	33.1	33.4	30.0	33.7	30.5
LaHabra	--	--	8.7	11.7	12.6(2)	13.6	14.6	8.9	17.0	14.5
Lennox	--	--	24.8	25.2	29.1	30.8	23.4	37.0	32.0	27.1
Long Beach	14.1	14.5	17.8	17.6	24.7	27.1	26.9	31.2	16.7	22.8
Los Angeles, Downtown	25.0	20.8	24.9	27.8	21.4	23.2	21.0	33.8	32.2	27.8
Pasadena	15.1	14.6	15.2	17.5	17.1	18.2	24.0	25.0	17.7	20.6
Pomona	--	--	18.0	18.4	19.4	25.3	26.7	32.7	28.9	25.4
Redlands	--	--	--	--	--	8.1	7.5	12.1	13.1	11.8
Reseda	--	--	16.9	16.2	18.0	23.3	21.3	27.7	23.3	23.5
Riverside	--	15.2	12.8	17.6	13.2	--	--	--	--	11.9
San Bernardino	4.9	1.9	7.7	10.9	16.5	13.1	12.4	14.7	--	12.8
West Los Angeles	16.4	15.5	20.1	19.7	15.8	25.3	21.0	28.7	25.5	18.2

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Table 6-14. OXIDES OF NITROGEN TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF 6 TO 9 a.m. DAILY AVERAGE CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a,11]
(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	3.5	5.0	4.2	8.0	7.9	10.2	10.6	8.2	11.1	9.8
Azusa	7.8	9.3	7.6	8.7	9.5	9.4	10.2	15.4	14.3	12.3
Burbank	13.3	14.5	17.5	15.3	18.0	26.5	27.8	25.1	27.5	23.5
LaHabra	--	--	--	--	5.1(2)	7.0	9.8	5.3	10.0	9.8
Lennox	--	--	19.5	19.4	22.5	24.1	19.0	25.9	24.0	19.7
Long Beach	9.5	10.1	12.7	13.5	17.1	18.1	18.3	23.4	10.5	16.4
Los Angeles, Downtown	19.9	17.1	20.4	22.7	16.8	18.5	17.0	27.5	27.1	21.9
Pasadena	10.1	10.1	10.4	12.2	12.1	11.8	15.7	16.5	11.1	13.3
Pomona	--	--	14.1	12.1	14.3	17.5	20.4	24.4	20.3	18.4
Redlands	--	--	--	--	--	4.2	4.5	7.6	8.2	7.5
Reseda	--	--	11.5	11.2	13.3	15.5	15.2	19.9	17.7	15.5
Riverside	--	13.8	9.2	14.0	10.7	--	--	--	--	8.5
San Bernardino	2.9	0.9	5.4	7.9	12.6	9.6	9.4	12.7	--	8.9
West Los Angeles	12.1	11.1	14.3	14.0	12.5	18.8	16.0	21.4	20.3	14.2

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

to the basinwide averages. Perhaps the most significant implication of these results is that delineation of the oxidant-hydrocarbon-NO_x relationships from atmospheric data alone is not easy. The most serious problem undoubtedly is the interfering effects from the varying meteorological conditions.

CONCENTRATIONS OF SULFUR OXIDES IN URBAN ATMOSPHERES

The sole purpose of including data on the atmospheric concentrations of sulfur oxides in this chapter is to present a more complete picture of the pollutants that may have a role in the oxidant formation process. Laboratory studies suggested that sulfur dioxide (SO_2) may either enhance or inhibit oxidant formation depending on the hydrocarbon reactant used.[41] Field studies, however, were inconclusive, leaving the question of the SO_2 role in oxidant

Table 6-15. OXIDES OF NITROGEN TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, ANNUAL AVERAGES OF DAILY MAXIMUM ONE-HOUR CONCENTRATIONS FOR ALL DAYS OF THE YEAR[a,11]
(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	10.7	11.1(3)	13.5(1)	13.3(2)	19.1	28.5	25.8	22.4	25.0	26.0
Azusa	12.6	12.5	10.7(2)	12.5	13.5	14.7	13.4	17.9	19.2	18.6
Burbank	31.0	27.7	33.3	32.1	36.7	45.8	42.0	43.0	42.8	40.5
LaHabra	--	--	17.9(1)	17.2	16.4(3)	22.2	16.1(1)	14.4	22.0	24.1
Lennox	--	--	36.7(1)	40.8	51.5	46.3	44.3	50.8	51.1	50.0
Long Beach	30.5	33.1	27.9	28.0	33.4	37.5	34.8	38.7	32.3	36.2
Los Angeles, Downtown	36.8	29.7	34.1	37.8	36.4	37.1	35.2	40.7	44.6	39.1
Pasadena	24.7	23.8	21.0	22.8	25.9	26.7	28.2	33.2	28.0	30.7
Pomona	--	--	22.3(5)	23.8	28.9	32.5	31.5	35.8	35.3	33.6
Redlands	--	--	--	--	--	9.4(3)	7.3(3)	11.9	16.9	17.2
Reseda	--	--	20.5(2)	25.3	27.5	30.0	27.2	31.3	34.8	35.6
Riverside	--	23.5(6)	19.2	17.9(1)	17.3	31.5(11)	--	5.3(11)	6.9(9)	16.6
San Bernardino	5.7	3.3(3)	9.7(8)	14.1(2)	16.2	13.2	11.5(3)	14.6(4)	16.9(7)	15.1
West Los Angeles	31.1	29.1	31.6	29.3	30.5	34.0	32.4	36.7	36.6	32.0

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Table 6-16. NITROGEN DIOXIDE TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF 6 TO 9 a.m. DAILY AVERAGE CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a,11]
(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	2.3	3.2	3.2	6.1	4.0(4)	4.0	6.1	4.7	5.3	4.1
Azusa	4.4	6.4	5.5	6.4	6.7	6.4	7.0	8.8	8.0	7.1
Burbank	5.8	6.8	8.7	7.7	10.9	12.6	13.4	11.7	12.8	9.7
LaHabra	--	--	--	--	--	4.1	6.4	3.2	5.6	5.3
Lennox	--	--	7.2	6.1	8.6	7.6	8.0	8.7	7.8	6.3
Long Beach	3.7	4.7	5.7	4.4	7.7	7.8	7.5	9.6	4.7	7.2
Los Angeles, Downtown	7.7	8.7	9.5	10.7	7.1	5.9	4.8	10.2	10.8	9.5
Pasadena	5.8	6.6	6.5	7.3	7.3	7.5	10.0	10.8	7.2	7.5
Pomona	--	--	8.2	7.6	7.8	8.5	10.3	11.3	10.2	8.5
Redlands	--	--	--	--	--	2.3	2.5	5.2	6.0	4.4
Reseda	--	--	7.0	6.8	8.4	8.5	9.5	11.8	9.5	7.9(1)
Riverside	9.2	7.6	5.9	8.0	7.1	--	--	--	8.2	4.5
San Bernardino	1.6	0.2	3.6	5.0	7.4	4.7	6.8	7.4	8.2	5.9
West Los Angeles	5.7	5.9	7.8	7.2	8.5	7.5	9.9	9.6	9.8	6.5

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

formation open. In addition to SO_2, sulfates also are present in the atmosphere as a result of photooxidation of SO_2. Sulfates occur in the form of constituents of the aerosol suspended in the air, and relate to the photochemical oxidant in that they are products of the same photooxidation process that results in oxidant formation. Thus, factors that tend to enhance oxidant formation also tend to enhance oxidation of SO_2 to sulfate.

Table 6-17. NITROGEN DIOXIDE TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, THREE-MONTH AVERAGES OF DAILY MAXIMUM ONE-HOUR CONCENTRATIONS FOR JULY, AUGUST, AND SEPTEMBER[a,11]
(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	4.6	5.7	5.1	9.8	7.2	8.5	10.3	8.2	9.1	6.8
Azusa	7.1	9.6	8.2	9.5	10.0	10.7	10.5	13.0	11.6	10.7
Burbank	10.5	12.3	13.7	12.1	16.1	19.5	22.6	19.0	21.1	14.7
LaHabra	--	--	6.0	8.2	6.8(2)	10.0	10.4	6.5	9.8	8.5
Lennox	--	--	11.1	10.2	14.1	12.7	11.8	14.0	12.0	8.8
Long Beach	9.0	9.5	10.5	9.1	15.2	16.0	16.6	17.3	11.5	12.3
Los Angeles, Downtown	12.2	13.7	15.6	17.4	12.2	11.1	10.2	16.3	17.6	14.6
Pasadena	9.6	10.3	10.4	10.9	10.9	11.8	16.7	18.2	12.7	11.8
Pomona	--	--	11.1	11.3	11.4	12.6	14.6	15.8	13.4	11.6
Redlands	--	--	--	--	--	4.7	4.8	8.2	9.4	7.3
Reseda	--	--	9.8	10.3	12.3	12.9	14.0	16.8	13.6	12.2
Riverside	11.6	9.6	9.0	10.1	9.5	--	13.6	9.0	10.8	6.1
San Bernardino	3.1	0.9	5.2	7.0	11.1	7.0	10.0	10.7	11.9	8.7
West Los Angeles	8.6	8.7	12.5	11.2	10.0	14.8	11.8	13.9	13.9	9.3

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Table 6-18. NITROGEN DIOXIDE TRENDS IN THE SOUTH COAST AIR BASIN, 1963-1972, ANNUAL AVERAGES OF DAILY MAXIMUM ONE-HOUR CONCENTRATIONS FOR ALL DAYS OF THE YEAR[a,11]
(pphm)

Station	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Anaheim	6.0	6.1(3)	6.3(1)	7.9(2)	8.6(1)	10.8	9.2	8.9	9.5	8.2
Azusa	8.3	8.8	7.9(2)	9.3	9.4	9.2	9.3	11.2	11.6	11.6
Burbank	10.9	10.5	12.8	13.3	16.2	19.1	16.8	16.3	16.6	14.0
LaHabra	--	--	7.7(1)	8.8	7.4(3)	10.1	8.1(1)	5.9	9.4	9.5
Lennox	--	--	12.1(1)	11.7	15.9	14.4	12.0	13.3	13.2	11.9
Long Beach	11.5	11.3	10.8	11.5	14.1	16.3	14.3	14.7	12.4	13.4
Los Angeles, Downtown	13.0	11.7	14.6	15.8	13.5	13.1	11.3	14.4	17.1	14.6
Pasadena	10.0	10.9	10.7	10.6	11.8	12.5	14.0	16.9	14.2	13.5
Pomona	--	--	11.3(5)	10.8	11.8	13.3	12.8	14.0	12.7	12.5
Redlands	--	--	--	--	--	4.8(3)	3.6(3)	6.4	8.3	7.5
Reseda	--	--	9.2(2)	10.5	11.8	11.9(11)	10.8(2)	12.7	13.0	12.9
Riverside	10.3(6)	8.9(1)	9.8	7.7(1)	8.6	8.4(11)	9.8(2)	7.9	9.0(1)	5.7
San Bernardino	3.1	0.8(3)	5.2(8)	7.7	9.1	6.4	7.4(3)	9.0(4)	9.1	8.4
West Los Angeles	10.4	10.3	13.5	12.3	12.2	14.5	12.1	13.2	14.6	12.4

[a] Numbers in parentheses indicate number of months of missing data. Dashes indicate stations were not operating or data were not reported.

Concentrations of sulfur oxides have been measured by several different methods, e.g., conductimetric, colorimetric, coulometric, etc. To date, the methods have not been evaluated adequately, and, therefore, the respective measurement results may not be directly comparable. Nevertheless, for the

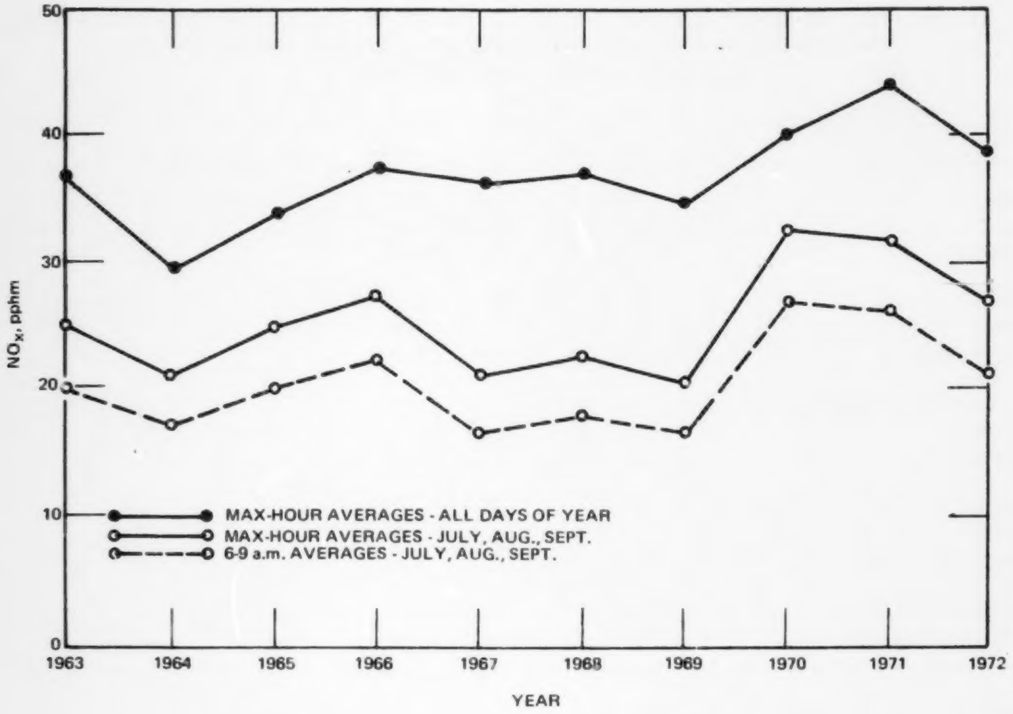

Figure 6-13. Oxides of nitrogen trends in Los Angeles, 1963-1972, 6 to 9 a.m. and maximum one-hour average concentrations.[11]

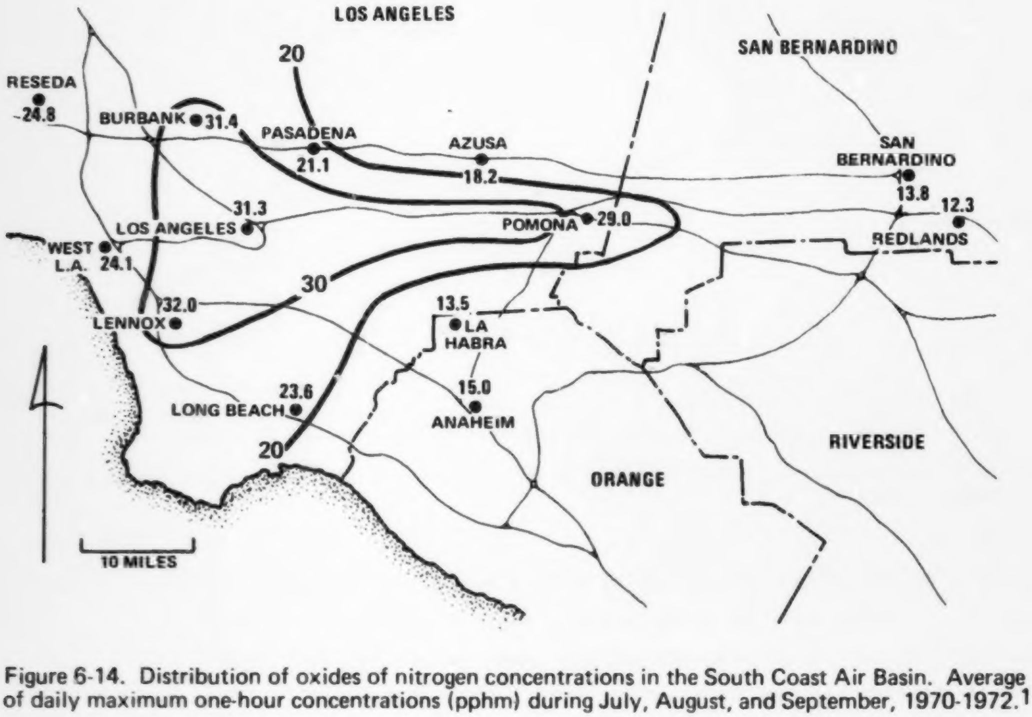

Figure 6-14. Distribution of oxides of nitrogen concentrations in the South Coast Air Basin. Average of daily maximum one-hour concentrations (pphm) during July, August, and September, 1970-1972.[11]

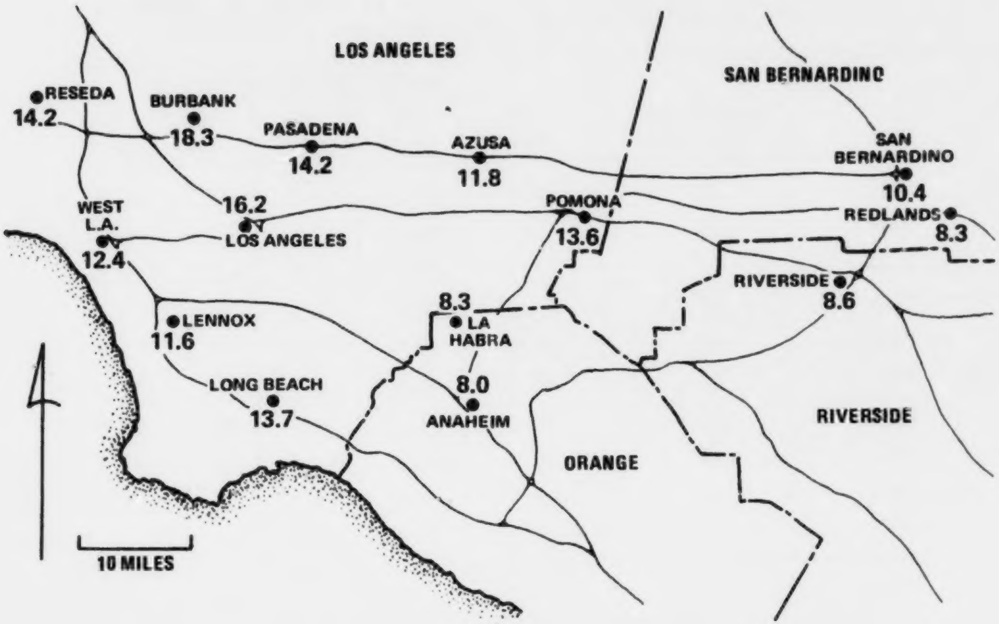

Figure 6-15. Distribution of nitrogen dioxide concentrations in the South Coast Air Basin. Average of daily maximum one-hour concentrations (pphm) during July, August, and September, 1970-1972.[11]

Table 6-19. VARIATION OF OXIDANT AND PRECURSOR CONCENTRATIONS WITHIN THE SOUTH COAST AIR BASIN, JULY, AUGUST, AND SEPTEMBER, 1970-1972

	Average concentration			
Station	NO_x, pphm	NO_2, pphm	HC, ppm C	O_x, ppm
Los Angeles	31.3	16.2	4.8	11.5
Anaheim	15.0	8.0	6.0	9.4
Azusa	18.2	11.8	6.4	23.3
San Bernardino	13.8	10.4	5.0	18.9
Basinwide average	22.3	12.1	5.0	14.8

purposes of this report, the data presented in this chapter are sufficiently informative.

The most extensive body of SO_2 concentration data has been obtained by the National Air Surveillance Network (NASN), a network of over 200 stations operated cooperatively by the Federal government and local health and air pollution agencies. The NASN data represent SO_2 concentrations in 24-hour integrated samples taken in downtown or center city areas only and analyzed by the West-Gaeke method. Data for nonurban atmospheres are very few. Tables 6-20 and 6-21 present the distributions of ambient SO_2 concentrations for urban and

Table 6-20. CUMULATIVE DISTRIBUTION BY PERCENT OF ANNUAL AVERAGE SULFUR DIOXIDE CONCENTRATIONS, URBAN SITES

Year	Number of stations	Percent of concentrations				
		<20 μg/m^3	<40 μg/m^3	<60 μg/m^3	<80 μg/m^3	<100 μg/m^3
1962	33	36.4	60.6	69.7	72.7	84.8
1963	26	15.3	30.7	49.9	57.5	76.7
1964	33	12.2	45.5	57.6	69.7	100.0
1965	34	29.4	44.1	64.6	76.4	100.0
1966	45	24.5	48.9	62.2	73.3	77.7
1967	47	21.3	48.9	68.1	74.5	100.0
1968	98	34.7	64.3	76.5	86.7	94.8
1969	109	39.5	73.5	86.4	94.7	97.4
1970	97	54.6	84.5	91.7	96.9	100.0
1971	71	66.2	90.1	98.5	100.0	

Table 6-21. CUMULATIVE DISTRIBUTION BY PERCENT OF ANNUAL AVERAGE SULFUR DIOXIDE CONCENTRATIONS, NONURBAN SITES

Year	Number of stations	Percent of concentrations		
		<10 μg/m^3	<20 μg/m^3	<30 μg/m^3
1968	5	40.0	100.0	100.0
1969	6	50.0	83.0	
1970	3	100.0		
1971	9	100.0		

nonurban atmospheres, respectively, based mainly on the NASN data. These data suggest that SO_2 concentrations have been declining in the period 1968-1971.

Table 6-22 presents a summary of the data taken by the CAMP stations. Such data represent SO_2 concentrations measured by continuous monitoring methods--a conductimetric method from 1962 to 1968, and a colorimetric one (West-Gaeke) since 1969.

Highest levels of SO_2 appear to occur in the New York City area. Recent data obtained by the New York Department of Air Control showed the yearly averages for the various sampling sites to range from 0.04 to 0.15 ppm in 1969 and from 0.05 to 0.11 ppm in 1970. Hourly concentrations recorded were as high as 1.0 ppm.

Diurnal and seasonal variations of ambient SO_2 are depicted graphically in Figures 6-16 and 6-17. Diurnal variations are caused partly by meteorological conditions and partly by variations in power use activities. Seasonal variations

Table 6-22. MAXIMUM CONCENTRATIONS OF SULFUR DIOXIDE FOR VARIOUS AVERAGING TIMES AT CAMP SITES, 1962-1968
(ppm)

City, averaging time	1962	1963	1964	1965	1966	1967	1968
Chicago, IL:							
1 hour	0.86	1.69	1.12	1.14	0.98	1.11	0.86
24 hours	0.36	0.71	0.79	0.55	0.48	0.65	0.51
1 month	0.18	0.33	0.35	0.27	0.27	0.32	0.27
1 year	0.10	0.14	0.18	0.13	0.09	0.12	0.12
Cincinnati, OH:							
1 hour	0.46	0.48	0.57	0.56	0.42	0.38	0.38
24 hours	0.11	0.11	0.18	0.15	0.14	0.07	0.08
1 month	0.04	0.06	0.06	0.06	0.05	0.03	0.03
1 year	0.03	0.03		0.03	0.03	0.02	0.02
Denver, CO:							
1 hour				0.36	0.26	0.17	0.24
24 hours				0.06	0.05	0.02	0.05
1 month				0.03	0.02	0.01	0.03
1 year				0.02	0.01		0.01
Philadelphia, PA:							
1 hour	1.03	0.85	0.84	0.94	0.72	0.77	0.88
24 hours	0.35	0.46	0.43	0.36	0.35	0.33	0.36
1 month	0.13	0.12	0.15	0.13	0.12	0.15	0.16
1 year	0.09	0.06	0.09	0.08	0.09	0.10	0.08
St. Louis, MO:							
1 hour			0.73	0.96	0.84	0.55	0.68
24 hours			0.26	0.19	0.18	0.21	0.16
1 month			0.08	0.06	0.06	0.05	0.05
1 year			0.06	0.05	0.04	0.03	0.03
Washington, D. C:							
1 hour	0.38	0.48	0.62	0.35	0.45	0.37	0.41
24 hours	0.18	0.25	0.22	0.20	0.25	0.15	0.18
1 month	0.10	0.11	0.09	0.08	0.10	0.07	0.10
1 year	0.05	0.05	0.04	0.05	0.04		0.04

also reflect variations in meteorology and power use. Thus, an analysis of 12 years of New York data showed that ambient SO_2 concentrations are inversely proportional to temperature.[42]

Sulfate data have been collected nationwide since 1957 by NASN. Such data consisted of measurements of sulfate (sulfuric acid and soluble sulfates) in suspended particulate matter collected from 24-hour integrated samples. The analytical method involves collection of aerosol from the air sample, water extraction of collected aerosol, and analysis of extract for sulfate by the methylthymol blue method. Tables 6-23 and 6-24 present the urban and nonurban distributions of annual sulfate averages. Figures 6-18 and 6-19 depict seasonal and long-term variations in ambient sulfate. Since the only data available are for 24-hour integrated samples, diurnal variations of sulfates are not known.

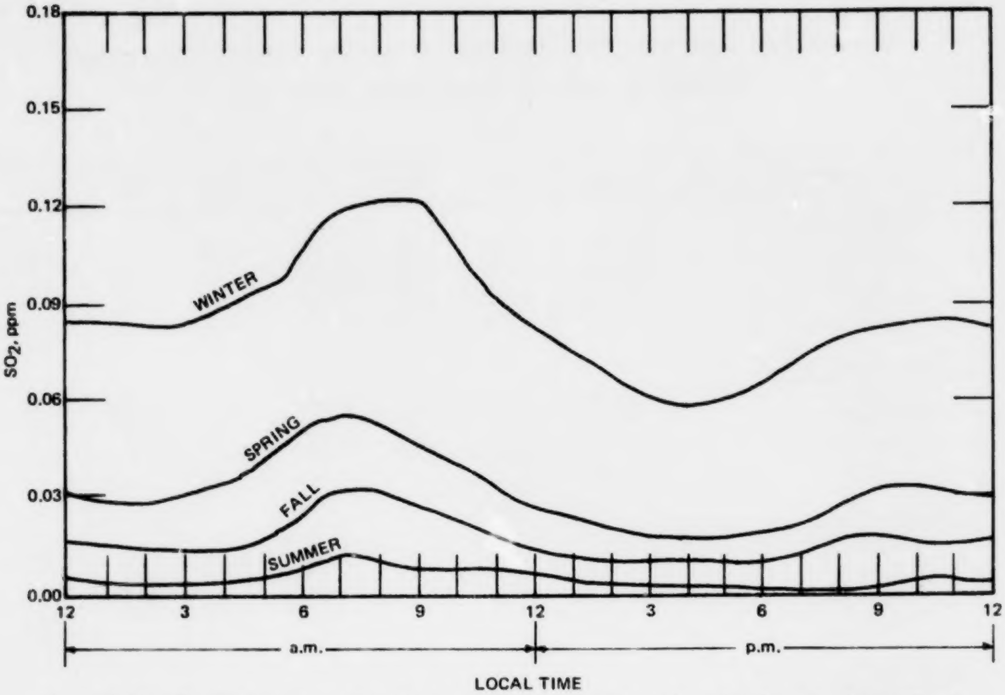

Figure 6-16. Diurnal patterns of sulfur dioxide concentrations (conductimetric data taken in Washington CAMP station in 1968).

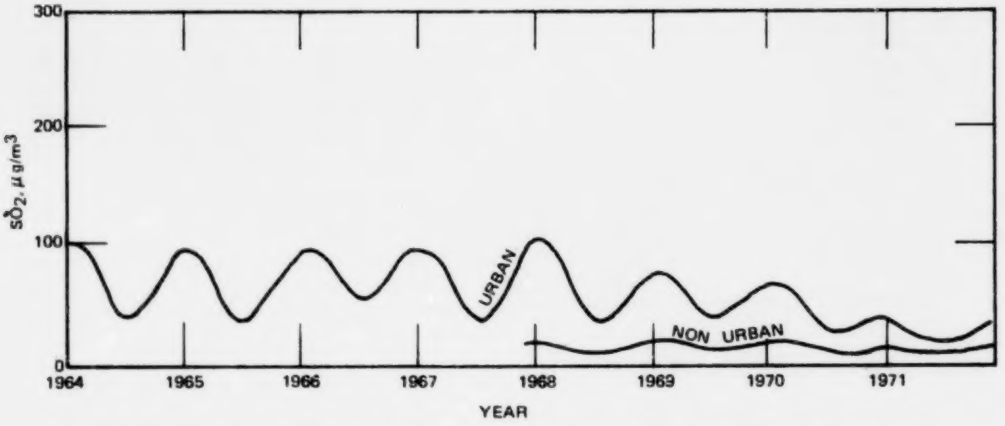

Figure 6-17. Seasonal patterns of sulfur dioxide concentrations (monthly NASN data for 1964-1971).

A few data on ambient levels of sulfuric acid were reported by Thomas.[43] Using an automatic instrument (conductivity) to simultaneously measure SO_2 and sulfuric acid, Thomas found sulfuric acid levels in Los Angeles and El Segundo, California, to range from 6.4 to 50.4 μg/m^3, and to constitute 2.3 to 13.4 percent of the SO_2 level.

Table 6-23. CUMULATIVE DISTRIBUTION BY PERCENT OF ANNUAL AVERAGE SULFATE CONCENTRATIONS, URBAN SITES

Year	Number of stations	Percent of concentrations					
		<5.0 μg/m^3	<10.0 μg/m^3	<15.0 μg/m^3	<20.0 μg/m^3	<25.0 μg/m^3	<30.0 μg/m^3
1957	33	17	57	87	93	97	100
1958	48	6	54	77	98	100	100
1960	61	13	38	72	93	100	100
1961	68	12	32	72	91	97	100
1962	79	16	52	81	96	97	100
1963	90	12	54	81	96	98	100
1964	100	23	66	84	95	97	100
1965	119	12	50	78	97	99	100
1966	99	21	53	84	98	99	100
1967	121	25	60	87	97	98	100
1968	146	21	60	85	96	99	100
1970	164	9	53	84	95	98	100

Table 6-24. CUMULATIVE DISTRIBUTION BY PERCENT OF ANNUAL AVERAGE SULFATE CONCENTRATIONS, NONURBAN SITES

Year	Number of stations	Percent of concentrations		
		<5.0 μg/m^3	<10.0 μg/m^3	<15.0 μg/m^3
1965	25	40	88	100
1966	27	48	96	100
1967	26	50	92	100
1968	25	48	88	100
1970	25	36	87	100

CONCENTRATIONS OF AEROSOLS IN URBAN ATMOSPHERES

As in the case of sulfur oxides, information on aerosol levels in urban atmospheres is included in this report only because atmospheric aerosol formation is related to oxidant formation in at least two respects. First, aerosol influences the overall oxidant formation (and/or destruction) process by promoting those reaction steps that occur on surfaces. Second, a part of the particulate material suspended in urban atmospheres is known to consist of products of the same photochemical activity that results in oxidant formation.

Most data on ambient aerosol concentrations come from the National Air Surveillance Network (NASN) and consist of total suspended particulate measurements by the high-volume sampler method.[44,45] Sizes of particles in collected

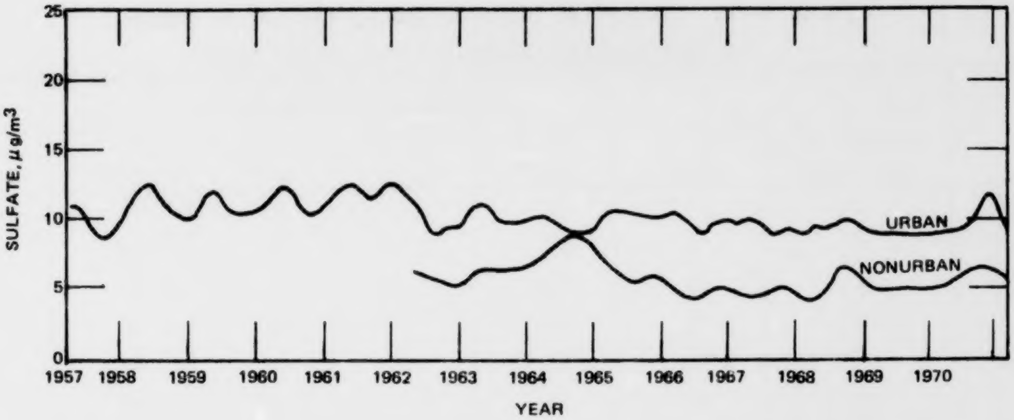

Figure 6-18. Seasonal patterns of sulfate concentrations (monthly NASN data for 1957-1970).

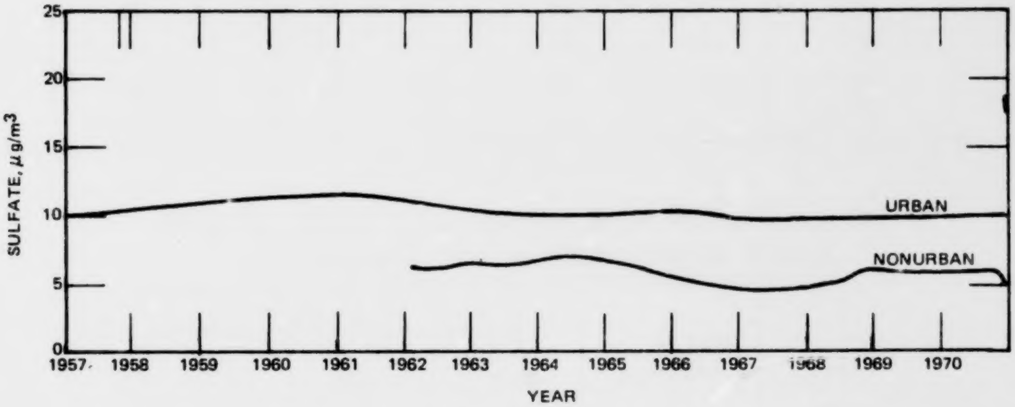

Figure 6-19. Long-term pattern of sulfate concentrations (monthly NASN data for 1957-1970).

samples range from a fraction of a micrometer to 100 micrometers. The NASN data generally relate to samples taken in the center-city commercial district. This portion of the community will generally not show annual average concentrations as high as those found in various industrial areas; however, they are among the higher area concentrations in a community. Annual concentrations in nearby suburban residential areas generally will be about one-half of those found in center-city areas.

A summary of data for several cities is given in Table 6-25. Concentrations of benzene-soluble organic particles are included as a measure of the organic particulate matter in the total sample. Table 6-26 shows the relation of population class of urban areas to particle concentration for the period 1958-1967, while Table 6-27 shows the frequency distribution of particle concentration in nonurban areas for the same period.

Whatever data are currently available on size distribution in suspended particles were for the most part obtained by the NASN Cascade Impactor Network.

Table 6-25. SUSPENDED PARTICLE CONCENTRATIONS (GEOMETRIC MEAN OF CENTER CITY STATION) IN URBAN AREAS, 1961-1965

Standard metropolitan statistical area	Total suspended particles		Benzene-soluble organic particles	
	μg/m³	Rank	μg/m³	Rank
Chattanooga	180	1	14.5	2
Chicago-Gary-Hammond-East Chicago	177	2	9.5	19.5
Philadelphia	170	3	10.7	12.5
St. Louis	168	4	12.8	4
Canton	165	5	12.7	5
Pittsburgh	163	6	10.7	12.5
Indianapolis	158	7	12.6	6
Wilmington	154	8	10.2	15
Louisville	152	9	9.6	18
Youngstown	148	10	10.5	14
Denver	147	11	11.7	8.5
Los Angeles-Long Beach	145.5	12	15.5	1
Detroit	143	13	8.4	28
Baltimore	141	14.5	11.0	10
Birmingham	141	14.5	10.9	11
Kansas City	140	16.5	8.9	23
York	140	16.5	8.1	34
New York-Jersey City-Newark-Passaic-Patterson-Clifton	135	18	10.1	16
Akron	134	20	8.3	30.5
Boston	134	20	11.7	8.5
Cleveland	134	20	8.3	30.5
Cincinnati	133	22.5	8.8	25
Milwaukee	133	22.5	7.4	42
Grand Rapids	131	24	7.2	44.5
Nashville	128	25	11.9	7
Syracuse	127	26	9.3	23
Buffalo	126	27.5	6.0	56
Reading	126	27.5	8.8	25
Dayton	123	29	7.5	40.5
Allentown-Bethlehem-Easton	120.5	30	6.8	50
Columbus	113	31.5	7.5	40.5
Memphis	113	31.5	7.6	39
Portland (Oreg.)	108	34	9.5	19.5
Providence	108	34	17.7	38
Lancaster	108	34	6.8	50
San Jose	105	36.5	14.0	3
Toledo	105	36.5	5.6	58
Hartford	104	38.5	7.1	46
Washington	104	38.5	9.4	21
Rochester	103	40	6.1	55
Utica-Rome	102	41	7.0	47
Houston	101	42	6.8	50
Dallas	99	43	8.8	25
Atlanta	98	44.5	7.8	36.5
Richmond	98	44.5	8.3	30.5
New Haven	97	46	7.3	43
Wichita	96	47	5.2	60
Bridgeport	93	50	7.2	44.5
Flint	93	50	5.3	59
Fort Worth	93	50	7.8	36.5
New Orleans	93	50	9.7	17
Worcester	93	50	8.2	33
Albany-Schenectady-Troy	91.5	53	6.6	52
Minneapolis-St. Paul	90	54	6.5	53
San Diego	89	55	8.5	27
San Francisco-Oakland	80	56	8.0	35
Seattle	77	57	8.3	30.5
Springfield-Holyoke	70	58	7.0	47.5
Greensboro-High Point	60	59	6.3	54
Miami	58	60	5.7	57

Table 6-26. DISTRIBUTION OF SELECTED CITIES BY POPULATION CLASS AND PARTICLE CONCENTRATION, 1957-1967

Population class	Number of cities with indicated average particle concentration ($\mu g/m^3$)										Total cities in table	Total cities in U.S.A
	<40	40 to 59	60 to 79	80 to 99	100 to 119	120 to 139	140 to 159	160 to 179	180 to 199	≥200		
>3 million	--	--	--	--	--	--	1	--	1	--	2	2
1-3 million	--	--	--	--	--	--	2	1	--	--	3	3
0.7-1 million	--	--	1	--	2	--	4	--	--	--	7	7
400,000-700,000	--	--	--	4	5	6	1	1	1	--	18	19
100,000-400,000	--	3	7	30	24	17	12	3	2	1	99	100
50,000-100,000	--	2	20	28	16	12	6	5	1	3	93	180
25,000-50,000	--	5	24	12	12	10	2	1	2	3	71	--
10,000-25,000	--	7	18	19	9	5	2	3	1	--	64	5453[a]
<10,000	1	5	7	15	11	2	1	2	--	--	44	--
Total urban	1	22	77	108	79	52	31	16	8	7	401	--

[a] Incorporated and unincorporated areas with population over 2500.

Table 6-27. DISTRIBUTION OF SELECTED NON-URBAN MONITORING SITES BY CATEGORY OF URBAN PROXIMITY, 1957-1967

Category	Number of cities with indicated average particle concentration ($\mu g/m^3$)				Total
	<20	20-39	40-59	60-79	
Near urban[a]	--	1	3	1	5
Intermediate[b]	--	5	6	--	11
Remote[c]	4	5	--	--	9
Total nonurban	4	11	9	1	25

[a] Near urban-although located in unsettled areas, pollutant levels at these stations clearly indicate influence from nearby urban areas. All of these stations are located near the northeast coast "population corridor."

[b] Intermediate-distant from large urban centers, some agricultural activity, pollutant levels suggest that some influence from human activity is possible.

[c] Remote-minimum of human activity, negligible agriculture, sites are frequently in state or national forest preserve or park areas.

Table 6-28 presents a summary of the 1970 data at six cities on a quarterly and annual basis. Table 6-29 presents a summary of data on occurrence of various chemical constituents in particles suspended in urban air.[46-49]

Table 6-28. QUARTERLY AND ANNUAL SIZE DISTRIBUTION OF PARTICULATE MATTER SUSPENDED IN AIR, 1970

City	Quarter	Number of samples	Average concentration, μg/m³	Average MMD,[a] μm	Average geometric standard deviation	Average mass of particulate, %	
						<1 μm	<2 μm
Chicago	1	4	97.8	2.31	10.41	37	48
	2	6	82.4	0.51	8.16	63	74
	3	7	98.3	0.62	5.88	61	75
	4	4	63.0	0.66	8.00	58	71
	Year	21	86.5	0.76	8.18	55	68
Cincinnati	1	1	61.9	0.37	5.71	72	84
	2	6	77.5	0.54	6.47	63	76
	3	7	88.9	0.77	5.15	57	72
	4	4	48.6	1.01	4.32	50	68
	Year	18	74.3	0.70	5.49	59	74
Denver	1	4	51.4	0.41	7.99	67	78
	2	5	51.4	0.19	10.22	76	85
	3	7	59.1	0.34	9.50	69	79
	4	5	80.7	1.02	10.65	50	62
	Year	21	59.7	0.40	10.50	65	75
Philadelphia	1	2	60.4	0.31	6.02	74	85
	2	6	50.9	0.26	11.21	71	80
	3	7	66.1	0.62	3.91	64	81
	4	5	56.8	0.55	6.34	63	76
	Year	20	58.5	0.47	5.65	67	80
St. Louis	1	5	81.2	0.97	6.61	51	65
	2	5	73.7	0.53	10.33	61	72
	3	9	76.5	0.89	5.69	53	68
	4	3	44.5	1.02	5.34	50	66
	Year	22	73.1	0.83	6.80	54	68
Washington, D.C.	1	5	53.0	0.47	5.98	67	79
	2	6	55.3	0.26	8.80	73	83
	3	6	73.5	0.51	3.95	69	84
	4	6	41.1	0.73	4.11	59	76
	Year	23	56.3	0.46	5.22	68	81

[a] Mass median diameter.

Particle concentrations in air have both diurnal and annual (seasonal) cycles, which for most cities are generally predictable in shape. A city with cold winters will experience a seasonal maximum in midwinter as a result of increased fuel use for space heating. A daily maximum in the morning, probably between 6 and 8 a.m., usually relates to a combination of meteorological factors and an increase in strength of sources of particulates, including automobile traffic.

Table 6-29. CONCENTRATION AND SIZE OF PARTICULATE CHEMICAL CONSTITUENTS IN URBAN AIR[43-46]

Component	Concentration, $\mu g/m^3$	MMD,[a] μm	Particles $\leq 1 \mu m$, %
Fe	0.6 - 1.8	2.2 - 3.57	12 - 35
Pb	0.59 - 3.2	0.25 - 1.43	59 - 74
Zn	0.1 - 1.7	0.58 - 1.79	14 - 72
Cu	0.08 - 0.4	0.87 - 2.78	16 - 61
Ni	0.04 - 0.11	0.83 - 1.67	28 - 55
Mn	0.02 - 0.17	1.34 - 3.04	13 - 40
V	0.06 - 0.14	0.35 - 1.25	41 - 72
Cd	0 - 0.08	1.54 - 3.1	22 - 28
Ba	0 - 0.09	1.95 - 2.26	20 - 31
Cr	0.28 - 0.31	1.5 - 1.9	45 - 74
Sn	0 - 0.09	0.93 - 1.53	28 - 55
Mg	0.42 - 7.21	4.5 - 7.2	17 - 23
SO_4^{2-}	1.9 - 13.1	0.1 - 0.66	65 - 85
NO_3^-	2.96 - 11.7	0.23 - 0.59	55 - 62
Cl	2.5 - 3.54	0.3 - 0.86	55 - 63
NH_4^+	4.0 - 9.5	0.35 - 0.53	65 - 82
PO_4^{2-}	0.22 - 0.31	3.7 - 3.9	18
Organic (pentane sol.)	3.2 - 17.6	0.07 - 0.31	58 - 98

[a] Mass median diameter.

In cities where photochemical pollution predominates, the maximum in concentration of particles in the range from 0.1 to 1 micrometer may come around noon, after the sun has had an opportunity to cause photochemical reaction. Under these conditions, the highest concentration of particles below 0.1 micrometer will come earlier, and there may be no clear trend for larger particles.

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CHAPTER 7. EMISSIONS OF OXIDANT PRECURSORS

INTRODUCTION

Hydrocarbons and nitrogen oxides are emitted to the atmosphere from both natural and man-made sources, the natural contribution being the major one. Natural hydrocarbon emissions arise mostly from biological processes, from trees, and from localized sources such as geothermal areas, petroleum and natural gas fields, coal fields, and natural forest fires. Worldwide emission rates for natural methane and for volatile terpenes and isoprene, for which measurements have been made, have been estimated to be 3 x 10^8 tons per year and 4.4 x 10^8 tons per year, respectively. Natural sources of nitrogen oxides are mostly biological processes, and worldwide emissions are approximately 5 x 10^8 tons per year.

Of the anthropogenic sources, combustion of fuels is by far the most important source of hydrocarbon and nitrogen oxide emissions. Additionally, hydrocarbon and nonhydrocarbon organic emissions also arise from the use of such organics as process raw materials.

From a pollution control standpoint, the distinction made between natural and man-made sources and the use of annual emission rates are not entirely satisfactory. Thus, anthropogenic emissions such as from leaking fuel lines, home appliances, etc., cannot be subjected to systematic control because of their "accidental" nature; therefore, from a control standpoint, such emissions are considered to be "natural." To generalize, classification of sources and emissions into "controllable" and "uncontrollable" may be more appropriate than the distinction now in use. Also, emission rate data reflecting annual or even daily averages are inadequate in that they mask diurnal variations in emission rate. Considering that only the morning to noon emissions are of main photochemical consequence, it is evident that ignoring the diurnal variation in emission rate does not permit equitable assessment of the various emission sources.

The comments made in the preceding paragraph are merely discussion points. The following sections in this report deal with the anthropogenic emissions only, and the emission rate data are presented as they are available, that is, mostly daily and yearly averages.

NATIONWIDE EMISSIONS

Hydrocarbons

Hydrocarbon emission sources generally are treated in terms of mobile and stationary sources because of the differing control strategies required for each in terms of engineering, technological, economic, and legal factors that must be taken

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into account. Total nationwide emissions of hydrocarbons and related organic compounds for the year 1968 are estimated to be 32 x 10^6 tons. Table 7-1 shows the distribution of this total by major source categories, including percent of relative contribution.[1] Motor vehicles (49 percent), industrial processes (14 percent), and solvent usage (10 percent) constitute by far the most significant sources. According to Mason et al.,[2] who reported similar information for the year 1966, approximately 63 percent of the total hydrocarbon emission arises from urban areas.

Table 7-1. ESTIMATES OF NATIONWIDE HYDROCARBON EMISSIONS BY SOURCE CATEGORY, 1968[1,a]

Source	Emissions					
	10^6 tons/yr			Percent of total emissions		
Transportation	16.6			51.9		
Motor vehicles		15.6			48.7	
Gasoline			15.2			47.5
Diesel			0.4			1.2
Aircraft		0.3			1.0	
Railroads		0.3			1.0	
Vessels		0.1			0.2	
Nonhighway use, motor fuels		0.3			1.0	
Fuel combustion--stationary	0.7			2.2		
Coal		0.2			0.7	
Fuel oil		0.1			0.3	
Natural gas		--[b]			--[b]	
Wood		0.4			1.2	
Industrial processes	4.6			14.4		
Solid waste disposal	1.6			5.0		
Miscellaneous	8.5			26.5		
Forest fires		2.2			6.9	
Structural fires		0.1			0.2	
Coal refuse		0.2			0.6	
Organic solvent evaporation		3.1			9.7	
Gasoline marketing		1.2			3.8	
Agricultural burning		1.7			5.3	
Total	32.0			100.0		

[a] These emission estimates are subject to revision as more refined information becomes available.

[b] Negligible.

Hydrocarbon emission estimates have been made for 22 major metropolitan areas in the United States.[1] Table 7-2 shows this information for each of the available areas. Perhaps of greater significance are the data given in Table 7-3, compiled from the study by Mason et al.[2] The most significant finding was that while transportation sources accounted for a higher proportion of total hydrocarbon emissions in these metropolitan areas than in the nation as a whole, the range was extremely wide: 37 to 99 percent.

Table 7-2. SUMMARY OF HYDROCARBON EMISSIONS FROM 22 METROPOLITAN AREAS IN THE UNITED STATES, 1967-1968[1]

Location[a]	Population	Area, mi^2	Emissions, 10^3 tons/yr
Los Angeles	7,100,000	41,000	1,270
Philadelphia	5,500,000	4,590	470
San Francisco	4,500,000	7,000	790
Detroit	4,090,000	2,680	480
Washington, D.C.	2,700,000	2,270	310
Boston	2,700,000	1,280	87
Pittsburgh	2,520,000	3,050	95
St. Louis	2,410,000	4,500	330
Hartford	2,290,000	2,650	120
Dallas	2,187,000	8,000	143
Seattle	2,010,000	15,000	170
Houston	2,000,000	7,800	292
Milwaukee	1,730,000	2,630	83
Cincinnati	1,660,000	2,620	55
Buffalo	1,300,000	1,470	130
Kansas City	1,230,000	3,200	230
Providence	1,200,000	1,000	54
Indianapolis	1,050,000	3,080	74
San Antonio	982,000	7,320	71
Dayton	880,000	2,310	64
Louisville	840,000	1,390	46
Birmingham	750,000	1,120	64

[a] Defined on the basis of Standard Metropolitan Statistical Areas; these may include substantial areas that are rural in nature and thus of low population density.

Table 7-3. PERCENT OF TOTAL AREA HYDROCARBON EMISSIONS BY SOURCE CATEGORY, 22 METROPOLITAN AREAS IN UNITED STATES, 1966[2]

Source category	Percent of total area emissions	
	Average	Range
Transportation	70.2	37-99[a]
Motor vehicles	66.9	
Fuel combustion	2.8	0-18
Power plants	0.1	
Industrial	2.2	
Domestic	0.5	
Process losses	19.9	1-63
Refuse disposal	7.1	0.4-26

[a] More recent estimates indicate that the maximum percent of total area hydrocarbon emissions in the transportation category is somewhat less than 99.

Nitrogen Oxides

The distribution of nitrogen oxide (NO_x) emissions by major source categories is indicated in Table 7-4.[3] Fuel combustion is the major cause of technology-associated emissions. In 1968 coal, oil, natural gas, and motor-vehicle fuel combustion accounted for over 18 of an estimated 20.6 million tons of man-made NO_x in the United States. Of the 10 million tons generated by stationary combustion sources, power plans emitted 4 million tons; industries, 4.8 million tons; and home and office heating plants, the remaining 1.2 million tons. Natural-gas-burning sources made the largest contribution of any fuel in the stationary source group. An estimated 8 million tons was emitted from transportation sources, 7 million tons of which was from motor vehicles. Industrial processes, solid waste disposal, and other miscellaneous sources accounted for about 2.5 million tons of NO_x.

Table 7-4. ESTIMATES OF NATIONWIDE NITROGEN OXIDE EMISSIONS BY SOURCE CATEGORY, 1968[3]

	Emissions					
Source category	10^6 tons/year			Percent of total emissions		
Transportation	8.1			39.3		
Motor vehicles		7.2			34.9	
Gasoline			6.6			32.0
Diesel			0.6			2.9
Aircraft[a]		N[b]			N	
Railroads		0.4			1.9	
Vessels		0.2			1.0	
Nonhighway		0.3			1.5	
Fuel combustion in stationary sources	10.0			48.5		
Coal		4.0			19.4	
Fuel oil		1.0			4.8	
Natural gas[c]		4.8			23.3	
Wood		0.2			1.0	
Industrial	0.2			1.0		
Solid waste disposal	0.6			2.9		
Miscellaneous	1.7			8.3		
Forest fires		1.2			5.8	
Structural fires		N			N	
Coal refuse		0.2			1.0	
Agricultural		0.3			1.5	
Total	20.6			100.0		

[a] Emissions below 3000 feet.

[b] N-not reported. Estimated less than 0.05×10^6 tons/year.

[c] Includes LPG and kerosene.

Relatively small quantities of NO_x are emitted from noncombustion industrial processes, mainly the manufacturing and use of nitric acid.[4] Even though total quantities may be small, high concentrations of NO_x can be emitted from some of these chemical processes. Electroplating, engraving, welding, metal cleaning, and explosive detonation can also be responsible for industrial NO_x emissions. The same is true with regard to the manufacture and use of liquid-NO_2-based rocket propellants.

NO_x emissions from 22 cities are summarized by source category in Table 7-5.

Table 7-5. PERCENT OF TOTAL AREA NITROGEN OXIDE EMISSIONS BY SOURCE CATEGORY, 22 METROPOLITAN AREAS IN THE UNITED STATES, 1966[2]

Source category	Percent of total area emissions	
	Average	Range
Transportation	42.6	23-74
Motor vehicles	36.3	
Other	6.3	
Fuel combustion in stationary sources	50.7	10-79
Power plants	23.0	
Industrial	23.8	
Domestic	3.9	
Process losses	5.2	1-21
Refuse disposal	1.5	0.1-5.8

Over 50 percent of the total NO_x emissions occur in highly populated areas; 60 percent of stationary source emissions and 45 percent of motor-vehicle emissions occur in urban areas.[3]

SOUTH COAST AIR BASIN EMISSIONS

Detailed emission inventory data are available for the Los Angeles, California, air basin.[5] The estimated average emission of contaminants into the atmosphere of the South Coast Air Basin is shown in Table 7-6. Total emissions in 1970 were 16,640 tons per day, including 3200 tons of organic gases, 235 tons of particulates, 1570 tons of nitrogen oxides, 315 tons of sulfur dioxide, and 11,300 tons of carbon monoxide.

A comparison of the emissions derived from stationary and mobile sources is shown in Table 7-7 and in Figure 7-1. The stationary sources were responsible for over 80 percent of the sulfur dioxide and more than 50 percent of all particulate emitted. Mobile sources emitted 71 percent of the organic gases and 77 percent of the nitrogen oxides.

Table 7-6. SOUTH COAST AIR BASIN, AVERAGE EMISSIONS OF CONTAMINANTS INTO THE ATMOSPHERE, 1970[5]
(tons per day)

Emission source	Organic gases by reactivity			Particulate matter	Oxides of nitrogen	Sulfur dioxide	Carbon monoxide
	High	Low	Total				
Stationary							
Petroleum							
Production		114	114	0.4	27.9	5.5	
Refining	5.0	40.0	45.0	5.0	22.0	50.0	5.0
Marketing	68.1	79.5	148		11.0		
Subtotal	73.1	234	307	5.4	60.9	55.5	5.0
Organic solvent users							
Surface coating	49.2	201	250	15.0			
Dry cleaning	6.1	26.1	32.2				
Degreasing	22.6	82.6	105				
Other	32.9	140	173	6.0		1.0	
Subtotal	110	450	560	21.0		1.0	
Chemical				0.5	0.2	115.0	
Metallurgical				21.3	3.0	32.9	3.0
Mineral		1.0	1.0	26.5	5.5	0.8	
Incineration							
Open burning (dumps)	0.2	2.0	2.2	0.7	0.3	0.1	4.0
Open burning (backyard)	1.2	13.0	14.2	4.7	2.3	0.2	34.4
Incinerators		1.2	1.2	1.2	1.2		1.3
Other	0.5	4.3	4.8	10.2	2.4		30.0
Subtotal	1.9	20.5	22.4	16.8	6.2	0.3	69.7
Combustion of fuels							
Steam power plants	0.2	6.8	7.0	7.8	135	40.9	
Other industrial	0.1	6.7	6.8	9.8	88.8	9.5	1.1
Domestic and commerical	0.2	0.2	0.4	9.8	60.1	0.6	0.4
Subtotal	0.5	13.7	14.2	27.4	284	51.0	1.5
Agriculture							
Debris burning	0.9	7.1	8.0	4.6	0.5		24.1
Orchard heaters		5.0	5.0	3.8		1.6	
Agricultural product processing plants	8.9	0.5	9.4	0.9			
Subtotal	9.8	12.6	22.4	9.3	0.5	1.6	24.1
Total, stationary sources	195	732	927	128	360	258	103
Mobile							
Motor vehicles							
Gasoline powered							
Exhaust	1200	401	1600	62.4	951	34.9	10,800
Blowby	51.3	16.9	68.2				
Evaporation	306	154	460				
Diesel powered		51.7	51.7	16.8	229	16.8	218
Subtotal	1560	623	2180	79.2	1180	51.7	11,000
Aircraft							
Jet driven	21.7	36.6	58.3	23.8	13.1	3.0	44.1
Piston driven	11.3	16.3	27.6	0.2	7.3	1.0	155
Subtotal	33.0	52.9	85.9	24.0	20.4	4.0	199
Ships and railroads		5.4	5.4	3.[illegible]	6.2	1.1	9.2
Total, mobile sources	1590	681	2270	107	1210	56.9	11,200
Grand total	1790	1410	3200	235	1570	315	11,300

Table 7-7. SOUTH COAST AIR BASIN, COMPARISON OF STATIONARY AND MOBILE SOURCES, 1970[5]
(tons per day)

Source	Total organic gases	Particulate matter	Nitrogen oxides	Sulfur dioxide	Carbon monoxide	Total emissions
Stationary	927	128	360	258	103	1,780
Mobile	2,270	107	1,210	56.9	11,200	14,800
Total	3,200	235	1,570	315	11,300	16,600
Stationary	29%	54%	23%	82%	1%	11%
Mobile	71%	46%	77%	18%	99%	89%

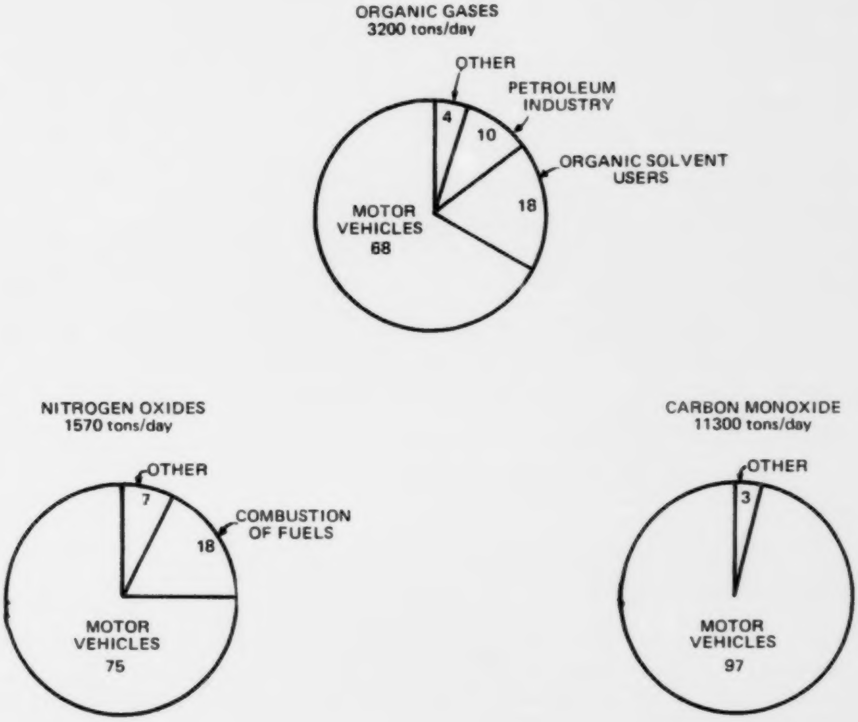

Figure 7-1. Percentage of emissions from major sources in the South Coast Air Basin,1970.[5]

Emissions trends in the United States are illustrated by those developed for the South Coast Air Basin. Tables 7-8 and 7-9 show such trends using emission data for 1960, 1965, 1970, and projected emissions for 1975 and 1980 also.

Table 7-8. SOUTH COAST AIR BASIN, HYDROCARBON AND NITROGEN OXIDE EMISSION RATES, 1960-1970[5,a]

Source	Emission rate, tons/day					
	Hydrocarbons			Oxides of nitrogen		
	1960	1965	1970[b]	1960	1965	1970
Combustion						
Mobile						
Air transport	19	40	86(33)	8	16	20
Road transport	2853	2410	2180(1560)	830	697	1180
Railways and navigation	--	1	5(0)	--	1	6
Stationary						
Power stations	20	20	7(0.2)	255	425	135
Industrial combustion			7(0.1)			89
Domestic and commercial heating			0.4(0.2)			60
Waste incineration	--	--	1(0)	5	1	1
Industrial						
Petroleum refining[c]	321	283	159(5)	6	60	61
Chemical	50	80	--	5	13	9
Mineral	--	--	1(0)			
Metalurgical	--	--	--			
Miscellaneous						
Forest fires and open burning	--	--	--	--	--	6
Surface coating, painting, etc.	310	411	250(49)	--	--	--
Service stations	--[d]	--[d]	148(68)	--	--	--
Dry cleaning	35	40	32(6)	--	--	--
Organic uses	206	256	173(33)	--	--	--

[a] The emission inventory on which this table is based[5] indicates the amount of fuel or the scale of operation for the sources listed.

[b] Numbers in parentheses indicate rates of "reactive" emission.

[c] Including evaporation losses in storage.

[d] Included in "Petroleum refining" emissions.

Table 7-9. SOUTH COAST AIR BASIN, PROJECTED HYDROCARBON AND NITROGEN OXIDE EMISSION RATES, 1975-1980[5]

Pollutant and source	Emission rate, tons/day			
	1975		1980[a]	
	Uncontrolled[b]	Controlled[c]	Uncontrolled[b]	Controlled[c]
Hydrocarbons				
Mobile	1690	335	1850	200
Stationary	210	140	225	149
Oxides of nitrogen				
Mobile	1290	535	1410	320
Stationary	385	357	420	392

[a] Projected 1980 hydrocarbon emission data are for "reactive" organic emissions.

[b] Assuming that no new abatement technology is applied.

[c] Assuming that appropriate abatement technology is applied.

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CHAPTER 8

RELATIONSHIPS BETWEEN AIR QUALITY AND EMISSIONS

INTRODUCTION

Air pollution legislation in the United States requires that numerical standards for ambient air quality be set and that, for achievement of these standards, appropriate emission control strategies be developed and implemented. Development of such control strategies, in turn, requires that the air quality be numerically defined as a function of emission rate. In the case of primary pollutants, e.g., carbon monoxide, the relationship between ambient concentration of pollutant and respective emission rate is controlled solely by the pollutant dispersion process. In the case of secondary pollutants such as the photochemical oxidants, the oxidant concentration-emission rate relationships are controlled not only by the dispersion of the hydrocarbon and nitrogen oxide emissions, but also by the atmospheric reactions of these oxidant precursors to produce oxidant.

In either case, the process of translating emission rates into air quality levels is an extremely complex one and cannot be quantified easily; that is, absolute levels of air quality cannot be calculated simply from emission rate, meteorology, and reaction rate data. This problem makes it extremely difficult to evaluate the degree of degradation of air quality caused in a source-free area as a result of initiation of human activity. However, most control practices to date have dealt with situations in urban areas, where specific interest has been in the degree of air quality improvement or degradation associated with application of a control measure or with expansion of human activity. In such control practices, fortunately, the problem is simplified to that of relating changes in air quality to changes in emission rate.

Relating changes in air quality to changes in emission rates for the purpose of developing numerical control strategies requires use of a model, that is, a premise that describes the physical and/or chemical mechanisms by which emissions affect air quality. Several types of models of varying complexity and inherent accuracy have been conceived and considered. Such models and their application in development of control strategies are discussed next.

ROLLBACK MODELS

A simple and intuitively obvious air pollution model is the one commonly referred to as "simple rollback."[1] This model assumes that the concentration of any stable pollutant in the air above an area is equal to the background concentration of that pollutant plus a fraction of the total emission rate of that pollutant in the area. Mathematically, the simple rollback model is described by Equation 8-1:

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$$C_i = B + ke \qquad (8\text{-}1)$$

where: C_i = ambient concentration of a specific pollutant at the i^{th} point

B = background concentration of pollutant at the i^{th} point

k = proportionality factor depending on meteorology, location of sources relative to i^{th} point, and the other factors that influence the source-receptor interaction at the i^{th} point

e = total emission rate from all sources in area.

Because of the difficulties in obtaining numerical values for k, Equation 8-1 was modified to relate changes in air quality (C_i) to changes in emission rate (e). Such modification led to Equation 8-2:

$$R = \frac{(GF)\ (PAQ) - (DAQ) + (B)[1-(GF)]}{(GF)\ [(PAQ) - (B)]} \qquad (8\text{-}2)$$

where: R = degree of emission rate reduction required in order to change air quality from the (PAQ) to the (DAQ) level

(GF) = growth factor, signifying the maximum potential for increase of emitter density

(PAQ) = present air quality, taken to be equal to the maximum observed level of the pollutant of concern in the atmosphere

(DAQ) = desired air quality, that is, the air quality standard

(B) = background level of pollutant, not subject to growth or control

Equation 8-2 appeared too complex, so it was simplified by setting (B)[1-(GF)]=0 and (GF)[(PAQ)-(B)]=(GF)(PAQ)-(B), resulting in Equation 8-3, which has been used in the United States to calculate control requirements.

$$R = \frac{(GF)\ (PAQ) - (DAQ)}{(GF)\ (PAQ) - (B)} \qquad (8\text{-}3)$$

Application of this formula is straightforward in the cases of primary pollutants. In the cases of a secondary pollutant such as ozone, reduction of ambient ozone levels obviously can be achieved only through control of the ozone precursors. It is also obvious that in order to calculate such control needs, it is necessary that (PAQ), (B), and (DAQ) of Equation 8-3 be known for the ozone precursors rather than for ozone. Of these, (B) and (PAQ) can be obtained through direct measurement of the background and total levels of ozone precursors. The "desired" level, however, of the ozone precursors (DAQ), that is, the precursor level corresponding to the air quality standard for ozone, obviously, is not measurable. Knowledge of the (DAQ) value requires that the dependence of ozone on its precursors be known quantitatively. Such dependence has been estimated, although not unequivocally; it was derived through analysis of atmospheric data as was discussed in Chapter 3. Specifically, it was found that for the oxidant concentration to be below 0.1 part per million (ppm), the nonmethane hydrocarbon concentration must be below 0.3 ppm carbon--no single numerical value could be justified. By extending this conclusion, it follows that for the oxidant to be below the standard of 0.08 ppm, the nonmethane hydrocarbon concentration must be below 0.24 ppm C. This last value has been used as the value for (DAQ) in Equation 8-3 to compute hydrocarbon control requirements for achievement of the oxidant standard.

The method outlined in the preceding paragraphs is the result of a first effort to relate air quality to emissions. As such, it has inadequacies, some of which were unavoidable because they represented the least damaging alternative among those available, and others that were merely uncertainties resulting from lack of specific backup evidence. On the basis of the comments and criticism voiced thus far, it appears that the most controversial parts of this early method are the method's "simple rollback" model and the technique for translating air quality in terms of ozone into air quality in terms of ozone precursors. For this reason, these two points of the method are examined critically.

The simple rollback model's premise that the concentration of man-made contaminants in air is proportional to the rate at which these contaminants are emitted in the air (Equation 8-1) is a rational one. Further, application of this model requires relatively little input data. For example, using this model, a usable relationship between air quality and emissions can be obtained without need for meteorological data. This combination of rationality and simplicity is what precipitated the choice of this model for use in the first efforts to relate air quality to emissions.

One inadequacy of the simple rollback model is that the model's validity cannot be verified experimentally. Such verification would require uniform reduction of emissions from all types of sources in a region--a situation that almost never occurs. Also, the model is questionable in the cases of those pollutants that are consumed or produced as a result of atmospheric reactions; in such cases, Equation 8-1 cannot be valid unless these reactions are of first order with respect to the pollutant.

Application of this model also requires that we know the maximum concentration that each pollutant can attain presently, since this maximum concentration is taken to be the measure of the air quality level (PAQ) corresponding to the present emission rate. Further, it is assumed that this maximum concentration is equal to the maximum observed concentration--an assumption that may not be sound since there may not be an air quality measuring station at the point of the highest pollutant concentration.

Finally, the simple rollback model is of limited usefulness because it treats the total of emission sources in a region as a single emitter. Thus, the model cannot predict the individual effects on air quality of emitters of different types (e.g., mobile and stationary). This limitation becomes evident in the cases where technological considerations dictate that control requirements be defined separately for different emitter types.

OTHER MODELS AND METHODS

The limitations of the simple rollback model and its applications have pushed air pollution workers to devise and use other models that were either simplified or extended versions of the simple rollback. Some of these models are mentioned briefly.

The "proportional model" is similar to the simple rollback except that it assumes additionally that the oxidant concentration in an area is directly proportional to the reactive hydrocarbon emission rate in that area. Thus, by this model, the hydrocarbon concentration does not necessarily need to be reduced down to 0.24 ppm C in order to ensure achievement of the oxidant standard; rather, the reactive hydrocarbon concentration needs to be reduced to a degree equal to the degree of oxidant reduction needed in order to achieve the oxidant standard.

The "variable source rollback" model is an extension of the simple rollback and is described by Equation 8-4:

$$C_i = B + k_{ij} \sum c_j \qquad (8\text{-}4)$$

where j designates the type of emission source, and k_{ij} is assumed to be the same for all source types. This model distinguishes the various types of emission sources and their contributions to C_i, and permits calculation of control requirements separately for each source type.

Under circumstances such that the k_{ij} cannot be assumed to be the same for all source types, Equation 8-4 becomes Equation 8-5:

$$C_i = B + \sum k_{ij}\, c_j \qquad (8\text{-}5)$$

and describes a model which, in principle, is more accurate--but also more complex--than the model described by Equation 8-4.

These more advanced air pollution models can make more detailed predictions than the simple rollback, which makes it possible to test their assumptions against experimental data. Thus, they allow one to predict the spatial distribution of various concentrations of pollutants on a given day, or for some long time period, which is not possible by simple rollback. These computed distributions can then be compared with measured air quality, and the models modified to obtain superior agreement. In addition, they can make short-term predictions for specific meteorological conditions, which can be compared with observed values. Because these more advanced models have this testing potential, they are being widely studied and tested. However, they also require vast data inputs of emission rates, traffic patterns, local meteorology, and topography. These requirements, thus far, have prohibited use of these models with advantage over the simpler rollback models.

The technique for translating air quality in terms of oxidant into air quality in terms of oxidant precursors also has problems. This technique is based on the use of the oxidant-hydrocarbon relationship (Figure 3-5) derived from aerometric data and, as discussed in Chapter 3, this relationship suffers from serious uncertainties. Thus, it is questionable whether the value 0.24 ppm C is an appropriate one to use for (DAQ) in Equation 8-3. It has been suggested that the oxidant-hydrocarbon relationship and a hydrocarbon standard consistent with the oxidant standard be derived from smog-chamber data (see Chapter 3). In view of the limitations of the aerometric data, the smog chamber method, despite its own shortcomings, is now being given serious consideration.

CALCULATION OF CONTROL REQUIREMENTS

The 1970 Amendments of the Clean Air Act directed the U.S. Environmental Protection Agency (EPA) to conduct a national program of research, regulation, and enforcement activities directed to prevent and control air pollution. The program includes generation of scientific evidence that could be used by the Federal and state governments as basis for development of emission control regulations. In pursuing these objectives, EPA developed techniques for estimating emission control requirements for achievement of the national air quality standard for oxidants. Specifically, EPA developed techniques for deriving numerical standards for motor vehicle emissions[1] and for calculating regional requirements for hydrocarbon emission control.[2]

The simplest method for deriving numerical emission standards is the one based on use of the rollback model, and more specifically, on Equation 8-3. Use of this equation requires that (1) a year be specified as the reference or "present" year, (2) a "target" year be specified, that is, the future year in which the air quality standard is expected to be achieved, and (3) numerical values be provided for (PAQ), (DAQ), (GF), (B), and emission rate for the reference year. The factor (PAQ) designates the highest pollutant concentration observed during the reference year. The growth factor (GF) is defined so that the product (GF) (PAQ) represents the highest pollutant concentration that would be expected to occur in the target year if no controls were to be applied.

To illustrate these calculations, Equation 8-3 is used to derive a numerical hydrocarbon emission standard for 1975 model year automobiles. For the purpose of comparing such a standard with the one legislated by the U.S. Congress, the same reference year will be used in these calculations as used by the Congress, i.e., 1970. Since 10 years are needed after 1975 to phase out the uncontrolled autos, it follows that the target year should be 1985. Numerical values for the various entries in Equation 8-3 are as follows.

By one estimate, the growth factor (GF) for the period 1970-1985 is 1.76. This value was based on a noncompounded growth rate of automobile population of 5.1 percent per year. The (PAQ), that is, the highest concentration of nonmethane hydrocarbon observed during 1970, is somewhat uncertain. It almost certainly occurred in the Los Angeles air basin; however, most of the Los Angeles data available are for total rather than nonmethane hydrocarbons. Based mainly on measurements conducted by EPA in Los Angeles, the highest nonmethane hydrocarbon concentration during 1970 is estimated to be 8 ppm C. The background nonmethane hydrocarbon concentration is taken to be 0.1 ppm C. Finally, the (DAQ), that is, the air quality standard for nonmethane hydrocarbon, has been determined by EPA to be 0.24 ppm C (see Chapter 3).

Using these numerical values, the degree of hydrocarbon emission control required is calculated, using Equation 8-3, to be 99 percent. This indicates need for much more drastic control of hydrocarbon emissions than the 90 percent control legislated by Congress. It must be stressed, however, that the above calculations provide only first estimates and, in some respects, they are almost certain to be inaccurate. Some open questions regarding these calculations are as follows.

The value used for the growth factor is at issue for a number of reasons. First, use of noncompounded rather than compounded growth data is probably incorrect. Second, it is questionable whether growth in terms of increase of automobile population affects the maximum hydrocarbon concentration as much as it has been assumed in the preceding calculations. It is logical that the center points of a city, where the maximum hydrocarbon concentration is likely to occur, would eventually get saturated with traffic and that further growth would raise pollutant levels in the suburbs rather than in the downtown areas. Finally, growth in the suburbs cannot be entirely without consequence. One may expect, for example, that suburbs located upwind from the center of the city may contribute to the pollutant buildup occurring in the downtown areas. All these effects point to a true (GF) value that lies somewhere between 1.0 and an upper limit value somewhat higher than 1.76.

The (PAQ) value used is also uncertain. This value is intended to represent the highest concentration in Los Angeles in 1970, and it is questionable whether the data available include this concentration. The data were limited to those taken during 1970, and were available only for the smog season of that year. Because of these limitations and because there is some uncertainty whether the sampling sites are properly situated, the (PAQ) value (0.8 ppm C) may be somewhat inaccurate.

The (B) value (0.1 ppm C) may be erroneously low. Background or uncontrollable levels of nonmethane hydrocarbons in Los Angeles may be as high as 0.6 ppm C--in which case no control could ever achieve the 0.24-ppm C standard.

Finally, the (DAQ) value (0.24 ppm C) is also subject to uncertainties as discussed in Chapter 3. For example, if emission control will result in considerably higher nitrogen oxide to hydrocarbon ratios in the future, as it is now expected, then a higher nonmethane hydrocarbon concentration (e.g., 0.5 ppm C) may still be sufficiently low to ensure achievement of the oxidant standard.

For the purpose of illustrating the effects of all these uncertainties on the calculated control requirements, such requirements were calculated using different sets of numerical data; results, including those obtained in the preceding calculations, are presented in Table 8-1.

Table 8-1. REQUIRED EMISSION REDUCTIONS BASED ON ROLLBACK MODEL WITH VARIOUS INPUT VARIABLES

Growth factor (GF)	Present air quality (PAQ), ppm C	Desired air quality (DAQ), ppm C	Background (B), ppm C	Required reduction (R), percent
1.76	8.0	0.24	0.1	99.0
1.5	8.0	0.5	0.1	96.6
1.0	6.0	0.5	0.1	93.2
1.5	6.0	0.75	0.1	92.7

These control requirements are more stringent than those imposed by the 1970 Amendments of the Clean Air Act. Further, if hydrocarbon emissions of nonautomotive origin cannot be controlled effectively, or if the concentration of uncontrollable (background) nonmethane hydrocarbons exceeds 0.1 ppm C, then control requirements for the automotive emissions should be even more stringent.

Numerical emission standards can be derived by applying the control requirement figures calculated in the preceding paragraph to the emission rate values for 1970. These values are 34.0, 4.1, and 4.0 grams per mile for carbon monoxide, hydrocarbons, and nitrogen oxides, respectively, resulting in a numerical standard for hydrocarbon emissions ranging from 0.04 to 0.3 gram per mile.

Compared with the calculation of national emission standards, the EPA-recommended method for calculating regional control requirements for hydrocarbon emissions is much simpler. Specifically, based on the oxidant-hydrocarbon relationship depicted in Figure 3-5, EPA has constructed a curve that relates the highest oxidant concentration observed during the reference year to the degree of nonmethane hydrocarbon concentration reduction required in order to ensure achievement of the oxidant standard. The resultant figure then, assuming zero levels of background oxidant and nonmethane hydrocarbon, is taken to be the degree of nonmethane hydrocarbon emission control required for the region under consideration. Obviously, the accuracy of these calculations depends on the accuracy of the curve in Figure 3-5 and on the validity of the 0.24-ppm C value that has been taken to represent the nonmethane hydrocarbon concentration corresponding to 0.08 ppm of oxidant. Both the curve in Figure 3-5 and the 0.24-ppm C value are of limited validity, as discussed in detail in Chapter 3.

REFERENCES FOR CHAPTER 8

1. Barth, D.S. Federal Motor Vehicle Emission Goals for CO, HC, and NO_x Based on Desired Air Quality Levels. J. Air Pollut. Contr. Assoc. 20:519, 1970.
2. Federal Register. Vol. 36, p. 15486-15506, Aug. 14, 1971.

CHAPTER 9

NATIONAL AND REGIONAL POLICIES FOR ABATEMENT OF PHOTOCHEMICAL AIR POLLUTION

HISTORY

In 1963, the U.S. Congress introduced and enacted Public Law 88-206, known as the Clean Air Act of 1963, outlining the Federal government's program for preventing and controlling air pollution in the United States. The Act emphasized a regional approach to air pollution control, and its implementation was assigned to the U.S. Department of Health, Education, and Welfare. In ensuing years, the Act was amended three times, in 1965, 1966, and 1970, resulting in considerable expansion of State and local control programs and strengthening abatement activities on the Federal level. Further, implementation of the Clean Air Act has become and remains the responsibility of the U.S. Environmental Protection Agency (EPA) and the Agency's Administrator, who reports directly to the President of the United States.

The control of motor vehicle emissions was initiated in the State of California in 1959 with the adoption of standards to control exhaust hydrocarbons and carbon monoxide. This was supplemented in 1960 with standards to control emissions resulting from crankcase blowby. The early California standards were goals requiring the demonstration of feasible technology before the establishment of implementation deadlines. Such scheduling was contingent upon the availability and certification of devices, systems, or modifications that would enable motor vehicles to meet the standards. In 1963, California adopted diesel smoke standards; however, as with the previous standards, there was no immediate implementation schedule. As a result of the certification of appropriate devices and systems, California required a first level of crankcase emission control effective with the 1963 models, improved crankcase emission control for 1964, and control of exhaust hydrocarbons and carbon monoxide in 1966.

The 1965 Amendments to the Federal Clean Air Act gave the Secretary of the Department of Health, Education, and Welfare the authority to control emissions from motor vehicles. Accordingly, on March 30, 1966, the initial Federal motor vehicle emission standards were adopted to become applicable with the 1968 models. The standards and procedures were similar to those that had been employed by California and required some control of exhaust hydrocarbons and carbon monoxide from light-duty vehicles and 100 percent control of crankcase emissions from gasoline-fueled cars, buses, and trucks. The term light-duty vehicle refers to self-propelled vehicles designed for street or highway use,

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weighing less than 6000 pounds fully loaded, and carrying no more than 12 passengers. Thus, the vehicle population is divided into two groups, light- and heavy-duty, which generally correspond to cars as opposed to buses and trucks.

On June 4, 1968, revised Federal standards that required more stringent control of hydrocarbons and carbon monoxide from light-duty vehicles, of evaporative emissions from the fuel tanks and carburetors of light-duty vehicles, and of exhaust hydrocarbon and carbon monoxide emissions from gasoline-fueled engines for heavy-duty vehicles were published. The fuel evaporative emission standards became fully effective with model-year 1971. The other standards applied to 1970 model-year vehicles and engines. Thus, with the introduction of 1970 models, the industry had reduced hydrocarbon emissions by almost three-quarters and carbon monoxide emissions by about two-thirds.

On November 10, 1970, standards were published applicable to 1972 model light- and heavy-duty vehicles and heavy-duty engines. The significant modification in these standards pertained to the method of evaluating the exhaust hydrocarbon and carbon monoxide emissions from light-duty vehicles. Improved methods of test operation, exhaust sampling, and gas analysis had been developed so that emission measurements would be more representative of actual discharges from in-use vehicles. On November 15, 1972, standards were published applicable to 1973, 1974, 1975, and 1976 light-duty vehicles and engines.

PRESENT POLICIES

The Clean Air Act in its present form authorizes EPA to carry on a national program of air pollution research and control activities. This program includes research on air pollution effects, research and development of control technology, control program support activities, financial and technical assistance to state and local agencies, development of air quality and emission standards, air pollution monitoring, and other activities related to these aims. The organizational structure of EPA, shown in Figure 9-1, reflects the Agency's specific responsibility areas.

Presently adopted pollution abatement policies are centered around a regional approach to air pollution control with emphasis on effort at the state and local government levels. EPA is responsible for establishing and sustaining a national research and development effort both within the Agency and extramurally through grant, contract, and cooperative activities. The Agency, under the Clean Air Act provisions, develops and issues air quality criteria for specific air pollutants that are known to result from man-made sources and are judged to have an adverse effect on public health and welfare. Such criteria documents must accurately reflect the latest scientific knowledge pertaining to the effects of such pollutants and to factors that might alter such effects.

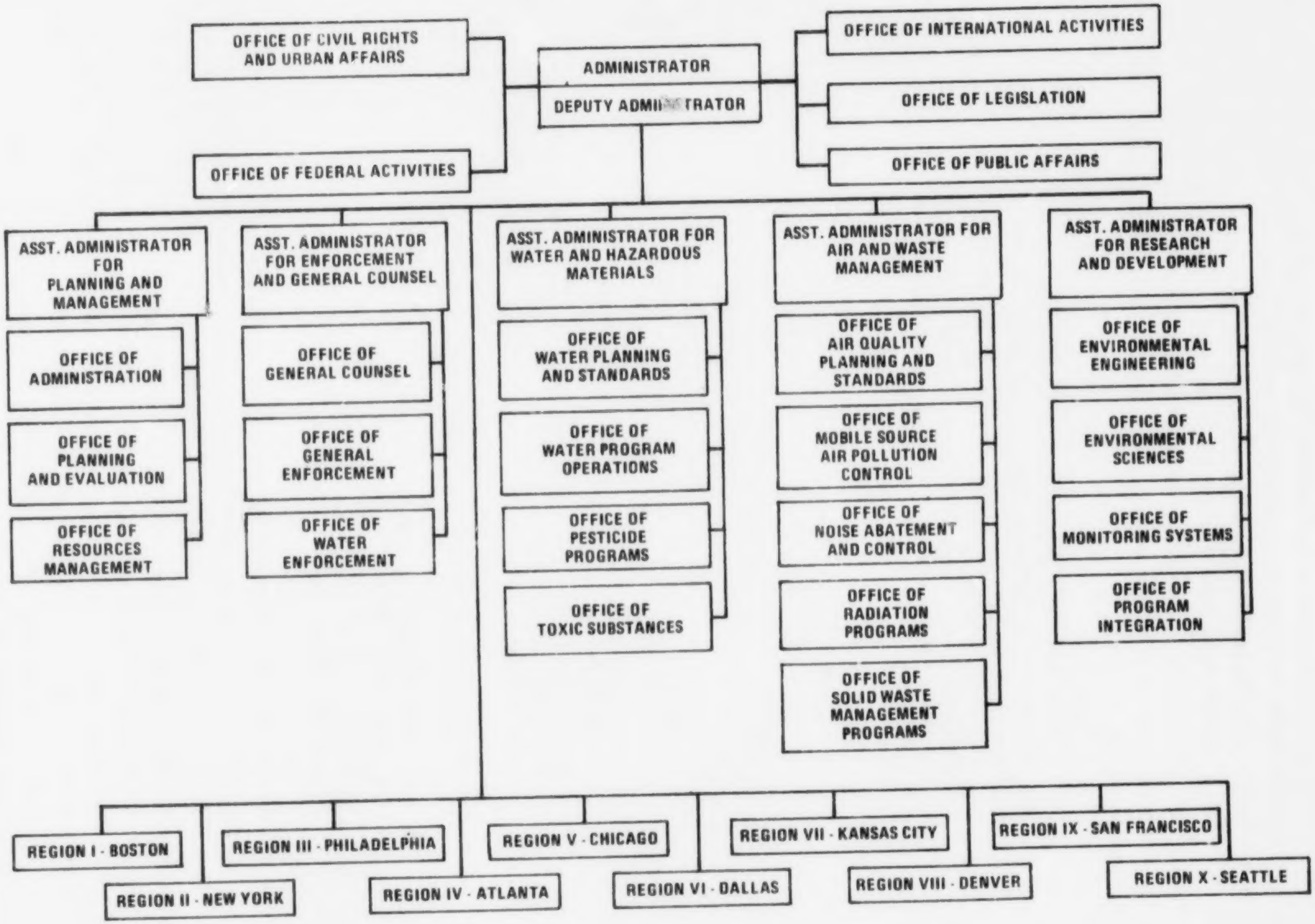
OFFICE OF CIVIL RIGHTS AND URBAN AFFAIRS
OFFICE OF FEDERAL ACTIVITIES
ADMINISTRATOR
DEPUTY ADMINISTRATOR
OFFICE OF INTERNATIONAL ACTIVITIES
OFFICE OF LEGISLATION
OFFICE OF PUBLIC AFFAIRS
ASST. ADMINISTRATOR FOR PLANNING AND MANAGEMENT
OFFICE OF ADMINISTRATION
OFFICE OF PLANNING AND EVALUATION
OFFICE OF RESOURCES MANAGEMENT
ASST. ADMINISTRATOR FOR ENFORCEMENT AND GENERAL COUNSEL
OFFICE OF GENERAL COUNSEL
OFFICE OF GENERAL ENFORCEMENT
OFFICE OF WATER ENFORCEMENT
ASST. ADMINISTRATOR FOR WATER AND HAZARDOUS MATERIALS
OFFICE OF WATER PLANNING AND STANDARDS
OFFICE OF WATER PROGRAM OPERATIONS
OFFICE OF PESTICIDE PROGRAMS
OFFICE OF TOXIC SUBSTANCES
ASST. ADMINISTRATOR FOR AIR AND WASTE MANAGEMENT
OFFICE OF AIR QUALITY PLANNING AND STANDARDS
OFFICE OF MOBILE SOURCE AIR POLLUTION CONTROL
OFFICE OF NOISE ABATEMENT AND CONTROL
OFFICE OF RADIATION PROGRAMS
OFFICE OF SOLID WASTE MANAGEMENT PROGRAMS
ASST. ADMINISTRATOR FOR RESEARCH AND DEVELOPMENT
OFFICE OF ENVIRONMENTAL ENGINEERING
OFFICE OF ENVIRONMENTAL SCIENCES
OFFICE OF MONITORING SYSTEMS
OFFICE OF PROGRAM INTEGRATION
REGION I - BOSTON
REGION II - NEW YORK
REGION III - PHILADELPHIA
REGION IV - ATLANTA
REGION V - CHICAGO
REGION VI - DALLAS
REGION VII - KANSAS CITY
REGION VIII - DENVER
REGION IX - SAN FRANCISCO
REGION X - SEATTLE

Figure 9-1. Organization of the U.S. Environmental Protection Agency (June 1975).

Following the issuance of criteria, EPA develops air quality standards (Table 9-1)[1] and promulgates regulations calling for implementation of such standards. Thus, each state is required to submit an acceptable plan that provides for implementation, maintenance, and enforcement of the air quality standards within the state. In the event that a state fails to submit an acceptable plan, EPA develops and promulgates such a plan. Implementation plans must also provide for the establishment of an air quality surveillance system meeting specified minimum requirements.

Table 9-1. NATIONAL AIR QUALITY STANDARDS FOR OXIDANT-OZONE, NITROGEN DIOXIDE, AND HYDROCARBONS[1]

Pollutant	Averaging time	California	Federal
Oxidant-ozone, ppm	1 hour	0.10[a]	0.08[c]
Nitrogen dioxide, ppm	1 hour	0.25[b]	-
	1 year	-	0.05[d]
Nonmethane hydrocarbons, ppm C	3 hours	-	0.24[e]

[a] One-hour average oxidant-ozone concentration must not exceed 0.10 ppm (based on health effects).

[b] One-hour average nitrogen dioxide concentration must not exceed 0.25 ppm (based on coloration).

[c] One-hour average oxidant-ozone concentration must not exceed 0.08 ppm more than once per year (based on health effects).

[d] Annual mean nitrogen dioxide concentration must not exceed 0.05 ppm (based on health effects).

[e] The average 6 to 9 a.m. nonmethane hydrocarbon concentration should not exceed 0.24 ppm C more than once per year. Achievement of this standard is not obligatory; it is offered merely as a guide to development of oxidant-ozone reduction strategies. (Based on role of NMHC in oxidant formation.)

EPA also develops emission standards for mobile and stationary sources. Unlike the stationary source standards, mobile source emission standards are subject to specific restrictions spelled out in the Clean Air Act. Thus, the hydrocarbon and carbon monoxide standards for 1975 and later and the nitrogen oxides standard for 1976 and later light-duty vehicles and engines must be such that they will require at least 90 percent reduction of the emission rates of the 1970 (for hydrocarbon and carbon monoxide) or 1971 (for nitrogen oxides) vehicles and engines. Finally, while EPA retains ultimate authority over regulations pertaining to emissions from new automobiles and aircraft and to fuel specifications, any state or political subdivision thereof may adopt or enforce standards and/or control requirements more stringent than those prescribed by EPA.

REFERENCE FOR CHAPTER 9

1. Title 42--Public Health, Part 410--National Primary and Secondary Ambient Air Quality Standards. Federal Register. 36(84):8186-8201, April 30, 1971.

CHAPTER 10
IMPLEMENTATION OF ABATEMENT POLICIES

STATUS OF STATE ABATEMENT PROGRAMS

Under the provisions of the Clean Air Act, as amended in 1970, States were required to submit plans to the U.S. Environmental Protection Agency (EPA) that would implement the national ambient air quality standards promulgated by EPA on April 30, 1971.[1] On August 14, 1971, EPA promulgated guidelines for preparation and submission of the State Implementation Plans (SIPs).[2] By May 30, 1972, EPA was required by the Act to approve or disapprove the SIPs, or portions thereof. By July 30, 1972, EPA was required to promulgate any portions of SIPs not yet approved.

On May 31, 1972, EPA published in the Federal Register the formal approval and/or disapproval of the SIPs.[3] Of the 55 SIPs (50 states plus American Samoa, Puerto Rico, Guam, the Virgin Islands, and the District of Columbia), only 14 were totally approved. The 41 remaining SIPs were disapproved in part because of the absence of, or deficiency in, one or more essential regulatory portions. In these cases, the EPA was required to propose and promulgate substitute regulations.

On June 14, July 27, and September 22, 1972, the EPA proposed regulations to correct the regulatory deficiencies of the SIPs. As of November 15, 1972, 13 states had corrected these deficiencies, thereby negating the need for the EPA to promulgate regulations for those states. Thus, as of December 31, 1972, there were 24 states for which EPA promulgation was not necessary.

After holding public hearings and reviewing comments, EPA promulgated regulations for 7 states on September 22, 1972, and for 7 additional states on October 28, 1972. Action on the remaining 14 states for which EPA promulgation is required is held in abeyance pending completion of hearings and review of public comments. If any of these states correct the regulatory deficiencies of their SIPs, EPA promulgation will be obviated. Also, EPA promulgation would be revoked for the aforementioned 14 states if necessary regulations were adopted by the states.

In those cases where controls on new automobiles and of new stationary sources are not expected to be sufficient for achievment of the oxidant standard, it is required that the states--or EPA if the states fail to comply--submit plans for transportation controls aiming at reduction of emissions by placing controls on older vehicles, by inspection-maintenance, and/or by reducing vehicle miles

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traveled. Such plans were to be submitted (for 38 regions) by April 15, 1973. The status of these transportation control plans may change due to matters now in litigation and other factors.

There have been several major impediments to the promulgation of SIPs and achievement of air quality standards. One such problem was the confusion caused by the discovery of inaccuracy in the nitrogen oxide measurement technique. Another such consideration is the Sierra Club suit against the EPA on the issue of nondegradation of air quality. By alleging that the Administrator violated the intent of Congress in his method of approving SIPs, the Sierra Club brings to issue policies on growth and development that may cause deterioration in air quality in areas where the national air quality standards are not exceeded. As a result of this suit, additional litigation and legislation are expected on this issue.

CONTROL OF HYDROCARBONS AND NITROGEN OXIDES FROM MOBILE SOURCES

EPA has been assigned responsibility for a number of programs and activities designed to abate pollution emanating from motor vehicles. Regulations establishing emission standards, testing procedures, and enforcement practices have been developed and promulgated to guide future actions. Table 10-1 lists mobile source emissions standards promulgated by EPA up to and through 1973.[3-5] Staff and contract personnel from the National Academy of Sciences are assessing the technological feasibility of attaining the 1975 and 1976 standards established in the legislation. EPA is expanding its capability to monitor industry progress, which is focussed upon optimization of carburetion and on add-on devices to clean up the internal combustion engine. Demonstration programs have been initiated concerning the feasibility of low-emission vehicles powered by conventional internal combustion engines. EPA is also directing a research and development program for low-emission power sources including the automotive gas turbine, the steam engine, electric drives, the free-piston engine, the Stirling engine, and the stratified-charge engine.

Federal authority for the control of vehicular emissions ends with the sale of new vehicles. States are encouraged to take action to ensure the continued operation and efficiency of emission control systems and other automotive systems that affect emissions. Reduced effectiveness of control systems after they leave the manufacturer may be due to a number of causes, including gross malfunction, improper adjustment, and deliberate removal or tampering.

A state may determine that its air quality in certain areas is such that a state control program for vehicle emissions is necessary to augment the degree of control provided by the Federal standards for new cars sold since 1968. Options available to the states, such as inspection and maintenance programs, may reduce carbon monoxide and hydrocarbon exhaust emissions.

Table 10-1. HYDROCARBON AND NITROGEN OXIDE EMISSION STANDARDS FOR NEW MOTOR VEHICLES AND ENGINES, 1973-1976[a]

Type of vehicle or engine	Model year			
	1973	1974	1975	1976
Light-duty gasoline vehicles and engines				
Exhaust hydrocarbons	3.4 g/mile	3.4 g/mile	0.41 g/mile[b]	0.41 g/mile[b]
Evaporative hydrocarbons	2.0 g/test	2.0 g/test	2.0 g/test[b]	2.0 g/test[b]
Exhaust NO_x (as NO_2)	3.0 g/mile	3.0 g/mile	3.1 g/mile[b]	0.4 g/mile[b]
Heavy-duty gasoline engines				
Exhaust hydrocarbons	275 ppm-hexane			
Exhaust [hydrocarbons + NO_x (as NO_2)]		16 g/brake-horsepower-hour		
Heavy-duty diesel engines				
Exhaust [hydrocarbon + NO_x (as NO_2)]		16 g/brake-horsepower-hour		
Light-duty diesel vehicles				
Exhaust hydrocarbons			0.41 g/mile[b]	0.41 g/mile[b]
Exhaust NO_x (as NO_2)			3.1 g/mile[b]	0.40 g/mile[b]
Light-duty gasoline trucks				
Exhaust hydrocarbons			2.0 g/mile	2.0 g/mile
Evaporative hydrocarbons			2.0 g/test	2.0 g/test
Exhaust NO_x (as NO_2)			3.1 g/mile	3.1 g/mile

[a] Test procedures are described in Reference 3.

[b] The EPA Administrator suspended effective date of the 1975 and 1976 standards (for requesting manufacturers) and established interim standards as follows:[4,5]

	1975	1976
Light-duty gasoline vehicles		
Exhaust hydrocarbons	1.5 g/mile	0.41 g/mile
Exhaust NO_x (as NO_2)	3.1 g/mile	2.0 g/mile
Light-duty diesel vehicles		
Exhaust hydrocarbons	1.5 g/mile	
Exhaust NO_x (as NO_2)	3.1 g/mile	

Other methods are available to check crankcase control devices, and these may be considered in addition to exhaust inspection. Recent model-year vehicles are equipped with evaporative control systems. Inspection and maintenance of these may be desirable, but little information on possible programs is currently available.

States must select methods for reducing vehicular emissions for both the control of existing air pollution and the prevention of future air pollution. Many practical difficulties may arise in implementing a statewide inspection and a maintenance system, but experience now being obtained by several states should be of assistance.

Five programs of the Coordinating Research Council, which are concerned with surveillance, maintenance, and inspection, are of particular significance here. These are Cooperative Air Pollution Engineering (CAPE) Projects 14 through 18.

Although it has been shown that various inspection and maintenance programs can reduce emissions of carbon monoxide and hydrocarbons, additional data are needed to demonstrate the cost and cost-effectiveness of such programs in practice.

In addition to inspection and maintenance of vehicles, other actions that may assist in reducing emissions from motor vehicles include the following:

1. Substitution of public transportation, in part, for the private automobile in urban areas.
2. Application of exhaust emission control devices to pre-1968 (preexhaust-controlled) light-duty vehicles.
3. Planning of freeways and traffic control systems to minimize stop-and-go driving and thus reduce emissions.

States must also consider long-range planning with respect to vehicle emissions. Some options of this type are listed below:

1. Planning for emergency actions to reduce vehicular emissions during periods when unfavorable weather conditions create an air pollution emergency.
2. Planning for governmental certification of maintenance and inspection personnel to protect the public from mechanics who inadvertently cause an increase in vehicular emissions through maladjustment or improper maintenance of engine components.

As an aid in estimating the quantity of vehicle emissions in a certain region, a procedure developed by the Federal government is available for use by states or communities. It requires only information concerning vehicle registrations or vehicle miles to arrive at estimated emissions.

CONTROL OF ORGANIC EMISSIONS FROM STATIONARY SOURCES

The Federal responsibility in the effort to control stationary source emissions is limited to approving or disapproving SIPs, issuing new source performance standards, that is, emission standards for new and significantly modified point sources, and issuing standards for hazardous pollutants. One group of new source performance standards for five industrial source categories were promulgated in 1971 (Group I in list below) and were revised in 1973. Standards for a second group of sources (Group II) were proposed in 1973. Groups I and II of the stationary sources considered thus far are listed below:

Group I: Fossil-fuel-fired steam generators
Municipal incinerators
Cement plants
Nitric acid plants
Sulfuric acid plants

Group II: Petroleum refineries
Secondary lead smelters
Iron and steel mills
Sewage treatment plants
Asphalt concrete plants
Brass and bronze ingot production plants
Storage vessels for petroleum liquids

Hazardous pollutants are also essentially a stationary source problem. Asbestos, beryllium, and mercury have been identified as hazardous pollutants and regulations were promulgated for such pollutants.

Of the state control activities, the most notable one is the development and adoption of Rule 66 in the County of Los Angeles, California, for control of organic solvent emissions.[6] The Rule classifies organics into photochemically reactive and nonreactive ones and imposes upper limits to allowable emission rates. The rest of the states have either adopted Rule 66 in its entirity or developed similar alternatives.

Methods used to control organic emissions are (1) substitution of materials, (2) operational or process changes, and (3) use of control equipment. Substitution of photochemically less reactive materials for reactive ones is used in cases where the organic emissions cannot be collected or incinerated by practical means. Such is the case, for example, with the organic solvent emissions from painting of buildings and structures. Control devices are classified into four categories based on the following control principles: incineration, adsorption, absorption, and condensation. Control methods used in some industrial processes are described in the following paragraphs.[7]

Petroleum Refining

Evaporation losses during storage are minimized by the use of floating-roof tanks, pressure tanks, and vapor conservation or recovery systems. Hydrocarbons from catalyst regenerators can be controlled by waste-heat boilers. Leakage from valves, pumps, and compressors can be reduced by systematic maintenance of connections and seals. Waste-water separators can be controlled by enclosing the separator tanks. Vapor recovery systems or smokeless flares are utilized to control hydrocarbon vapors from blowdown systems. Stripping gases from acid treating, doctor treating, and caustic treating and air-blowing effluents can be controlled by incineration.

Gasoline Distribution Systems

Vapors emitted during the loading of gasoline tank trucks can be collected and delivered to a vapor disposal system. The collection system consists of a tight-fitting hatch and a vapor delivery line. For top-loading tanks, the vapor delivery line is an annular space around the gasoline delivery line. For bottom-loading tanks, the vapor line is a separate line connected at the top of the tank. Vapors can be delivered to a gas-blanketed vapor holder and used as fuel in boilers and heaters where the load rack is adjacent to the refinery. For storage and loading facilities at other locations, packaged vapor recovery units have been developed in which the vapors are compressed and reabsorbed in gasoline.

Chemical Plants

The principal raw materials for synthetic organic products are derived mostly from petroleum and to a lesser extent from the by-products of the coking of coal. These materials are processed through the following types of conversions: alkylation, hydrogenation, dehydrogenation, dehydration, esterification, halogenation and dehalogenation, oxidation, nitration, and polymerization. Waste gases from processing units can be collected and delivered to a burner, to a gas holder, or into a fuel header system. Waste gases from units producing chlorinated hydrocarbons can be processed to recover by-product hydrochloric acid. Direct-flame and catalytic afterburners are used to eliminate organic vapors and mists from many off-gases.

Paint, Lacquer, and Varnish Manufacture

Emissions from paint and lacquer manufacture occur during mixing, grinding, and thinning operations. Varnish ingredients must be "cooked" to promote such reactions as depolymerization, esterification, isomerization, melting, and bodying. Emissions contain fatty acids, aldehydes, acrolein, glycerol, acetic acid, formic acid, and complex residues of thermal decomposition. Control systems consist of condensers, scrubbers, and afterburners.

Rubber and Plastic Products Manufacture

Emissions from rubber product manufacture occur during heat plasticization, chemical plasticization, and vulcanization. Control techniques include carbon adsorption, direct-flame and catalytic incineration, and reformulation to nonphotochemically reactive materials. In plastic products manufacture, emissions can occur from curing ovens, particularly when dioctyl phthalate is used as a plasticizer. Such mists can be controlled with high-energy scrubbers or with afterburners.

Surface Coating Applications

Emissions of hydrocarbons from the application of paint, varnish, and similar coatings are due to the evaporation of the solvents, diluents, and thinners. Where controls are required, reformulation with nonphotochemically reactive solvents is a method of control. Afterburners have been used to control emissions from paint bake ovens. These ovens can sometimes be redesigned to reduce the volume of gases to be handled, effecting considerable savings. Heat recovery systems can lower operating costs by reducing fuel requirements.

Degreasing Operations

Most vapor-phase degreasers use chlorinated hydrocarbon solvents, principally trichlorethylene. Less photochemically reactive 1,1,1-trichloroethane (methyl chloroform) and perchloroethylene can be substituted. Activated-carbon adsorbers can be used to control emissions in some applications. Solvent emissions can be minimized by elimination of drafts, good drainage of work items, controlled speed of work entering and leaving work zone, and covering of tank whenever possible.

Dry Cleaning

Dry cleaning is done by two processes: those using petroleum solvents and those using perchloroethylene or other halogenated solvents. In plants using perchloroethylene, vapor is recovered by water-cooled condensers, which may be followed by activated-carbon adsorbers. The value of the solvent makes recovery economically feasible. Plants using petroleum solvents can be controlled, if necessary, by using solvents reformulated to be nonphotochemically reactive. Control by activated carbon may be feasible.

Stationary Fuel Combustion

Hydrocarbons may be emitted if combustion is not complete. When properly designed and operated, stationary fuel combustion equipment is not a serious source of organic emissions.

Metallurgical Coke Plants

The hydrocarbons from the coking of coal are collected to recover by-products. Emissions occur during charging operations and from improperly fitting doors and other leaks. Emissions during charging can be reduced by steam-jet aspirators in the collection pipes. Self-sealing doors and good maintenance programs can reduce emissions.

Sewage Treatment Plants

Primary sewage plants emit hydrocarbons from the screening and grit chambers and from the settling tanks. Activated-sludge plants emit gas from the aeration tanks. Trickling filter plants emit organic gas from the filters, the clarifiers, and the sludge-digestion tanks. Control of emissions can be accomplished by covering or enclosing the various treating units and oxidizing or combusting the effluent gases.

Waste Disposal

Burning of waste materials can cause emissions of hydrocarbons. Open burning and inefficient incinerators are the predominant sources of such emissions. Control can be achieved by using multiple-chamber incinerators, by disposing of the waste in sanitary landfills, or by recycling.

Miscellaneous Operations

Emissions from deep fat fryers and coffee roasters can be controlled by afterburners. Fish cookers can be controlled by condensers. Evaporators of liquids from fish processing can be controlled by condensers and scrubbers and fish meal driers by scrubbing with chlorinated water. Noncondensible gases from charcoal manufacturing can be burned.

CONTROL OF NITROGEN OXIDES FROM STATIONARY SOURCES

Regulatory measures regarding nitrogen oxide (NO_x) emissions from stationary sources are limited to the Federal new source performance standards discussed in the preceeding section of this report and to state regulations as required for implementation of the air quality standard for nitrogen dioxide (NO_2). Commercially demonstrated control techniques used in the United States with varying degrees of success are described in the following paragraphs.[8]

Combustion Modification

Two-stage combustion in oil- and gas-fired boilers has reduced NO_x emissions from power plant boilers by 30 to 50 percent. Low-excess-air operation has reduced NO_x emissions from oil- and gas-fired power plant boilers by 30 to 60 percent, depending upon the percentage of excess air, the design of the boiler, and the type of firing. Tangential firing can produce reductions in NO_x of up to 50 percent compared with front-fired or opposed-fired furnaces.

A modified two-stage combustion technique combined with low-excess-air firing has reduced the stack-gas NO_x concentration emitted by two 750-megawatt gas-fired power-plant boilers from 1500 to 175 parts per million (ppm). Nominal costs with no decrease in generating capacity were reported by the company.

Emissions of NO_x from gas turbine engines is currently a major problem. Since standards are in the process of being determined for NO_x levels from turbines, there is considerable effort being expended to define the emissions picture for these sources. The major control method in use at the present time is steam or water injection into the combustor section of the turbine. Since this method requires ultrapure water, its applicability is seriously limited and a major effort is underway by the turbine industry to develop dry control methods. These dry methods generally involve hardware modification in the area of the combustor. The combustors are redesigned to incorporate staged combustion effects and internal combustion gas recirculation for NO_x reductions.

Diesel engine emissions have been under considerable study by the automotive industry and many of the control techniques for mobile sources also apply to stationary sources. The precombustion chamber concept, developed many years ago to control peak engine pressures, has been found to be a very effective NO_x control device. Essentially this concept is a staged combustion process: a rich fuel mixture is ignited in a separate chamber and then forced into the cylinder along with additional air to complete combustion. Other methods for reduction of NO_x in stationary diesels are: reduced fuel injection rate, increased retardation of timing water injection, exhaust gas recirculation, and lower compression ratio.

Most of the current work with piston engines is directed at mobile sources, but stationary engine work is in planning based on results from automotive studies.

All of the above approaches are based on considerations of chemical equilibrium and reaction rate. They involve reduction of peak gas temperatures, trends away from oxidizing and toward reducing atmospheres, and changes in the time-temperature history of the combustion gases. These approaches are all commercially demonstrated for large oil- and gas-fired boilers, but are yet to be demonstrated for large coal-fired boilers.

Changes in Fuel or Energy Source

Generation of electricity through the use of nuclear energy is projected to grow in the future. Essentially no NO_x is emitted since this source of energy does not depend on the combustion of fossil fuels. In 1968, 12 billion kilowatt-hours of electric power generated from nuclear energy was reported in the United States; optimistic sources project 3000 billion kilowatt-hours by 1990.

Waste Disposal Technique

Substitution of sanitary landfills for open burning has proved to be a commercially demonstrated control technique in certain areas of the country.

Chemical Sources

Nitrogen oxides from chemical sources may be decolorized by catalytic reduction using fuels such as natural gas or hydrogen. Such reactions are exothermic and much heat is generated. Because of practical considerations, such as catalyst life and the temperature limitations of structural materials, only the process of decolorization by reduction to NO has been uniformly successful.

Catalytic reduction of NO_2 to NO is not a true control technique; it merely decolorizes the stack gas. Stack velocities and normal atmospheric turbulence contribute to rapid dilution, with increasingly slow rates of oxidation of NO by air. Photochemical reactions in the atmosphere can, however, oxidize these small NO concentrations to NO_2.

Other Techniques

Other control techniques that have had limited commercial success or of only speculative nature include energy substitution, source relocation, catalytic reduction of NO_x to nitrogen, caustic scrubbing, incineration of NO_x to nitrogen, steam and water injection, flue-gas recirculation, stack-gas treatment, and adsorption on molecular sieves.

ESTIMATION OF EMISSION RATES

For an accurate air pollution survey, whether for a single source or for a metropolitan area, pollutant emissions must be identified by type and quantity. This determination--together with meteorological air quality and effects sampling programs--fulfills the requirements for local, state, and Federal air pollution control activities.

Ideally, the determination of emission rates should include analysis of emission effluents from all sources of interest, but this is impractical when an air pollution survey must cover a large area containing thousands of sources. For this reason, emission rates are estimated using emission factors, that is, emission rates per unit of source magnitude. Such emission factors have been determined for all sources of significance in the United States and are used here to illustrate the computational procedure used to estimate emission rates for single sources or for a region.

Regional Vehicular Emissions

The basic method for predicting total motor vehicle emissions is to multiply emission factors, modified to represent on-the-road emission rates, by the vehicle miles of travel (VMT). The National Air Pollution Control Administration (an

EPA predecesor agency) used a similar simplified approach for estimating nationwide vehicle emissions.[9] Two types of vehicle operating conditions were assumed, urban and rural. All urban travel was assumed to be at an average speed of 25 miles per hour beginning from a "cold start"; i.e., the vehicle was assumed not to have been driven prior to beginning travel at the urban driving speed. All rural travel was assumed to be at an average speed of 45 miles per hour, beginning from a "hot start." In this case, the vehicle was assumed to have been operated before being driven at the rural speed. The emission factors were then adjusted for these average speeds. A further seasonal adjustment was made. No correction was made for altitude. The national miles of travel for passenger cars, trucks, and buses were taken from Highway Statistics.[10] The future projections of national vehicle miles of travel were estimated from the "medium" projections presented in Resources in America's Future.[11] It should be noted that forecasts made prior to the 1970 census assumed a higher growth rate than is now occurring.[12] The total VMT were divided into passenger car and truck miles and further into rural and urban driving, according to the assumed weighting. The national emissions for each pollutant were then obtained by multiplying these vehicle miles traveled by the appropriate emission factor.

Subsequently, a method that modified this approach on a regional basis was developed from appropriate emission factors and the motor vehicle population and driving pattern for the particular region.[13] Total vehicle travel is determined from regional transportation studies, local traffic surveys, U.S. Department of Transportation data, and Federal Highway Administration publications.[14-16] The statistics available from Highway Statistics[10] include, by state, miles of public roads and streets, average daily traffic loads, number and type of vehicles registered, and estimated motor vehicle (passenger and truck) travel by highway system. Also included are motor fuel consumption and speed trends by roadway type and vehicle type. Highway Statistics assumed that since the total emissions from all gasoline-powered motor vehicles in a region is a function of the vehicle emission factors, the vehicle miles traveled in the region, and the percent travel that is urban or rural, a proportional relationship could be made to obtain regional emissions from the average national emissions. This assumption is valid if the regional vehicle mix of ages, types, makes, and deterioration rates, as well as the percentages of road types, average speeds, and miles of travel, are the same as the national average. The following equations are used to obtain regional emission estimates:[17]

$$TE = UE + RE$$

$$UE = (UF)\ (VMT)\ (a)\ (k)$$

$$RE = (RF)\ (VMT)\ (1-a)\ (k)$$

where:

TE = Total emission of a pollutant, tons/year
UE = Urban emission of a pollutant, tons/year
RE = Rural emission of a pollutant, tons/year
UF = Urban emission factor, g/mi
VMT = Vehicle miles of travel
a = fraction of travel that is urban
k = 1.1023×10^{-6} ton/g (conversion factor)
RF = Rural emission factor, g/mi

The emission factors (for both cars and trucks) needed for the calculation are presented for each pollutant (hydrocarbons, carbon monoxide, and oxides of nitrogen) by year and by urban and rural driving. The VMT and the fraction of urban travel are to be obtained from local traffic studies. (Vehicle miles of travel and projections for future years for most cities are available as a result of the Federal Aid Highway Act of 1962, which required cities with populations over 50,000 to initiate transportation studies in order to qualify for Federal aid for road construction.)

This simplified method can be updated by using the latest emission factors given in Reference 18. A sample calculation for a metropolitan area is shown in Tables 10-2 to 10-4. Adjustment of the emission factor for the speeds of the roadway type, with the miles of the roadway type, vehicle type (light-duty or heavy-duty), and the respective vehicle miles traveled would provide an even more accurate calculation of emissions.

The accuracy of the gasoline-powered motor vehicle emissions prediction is not only dependent on the emission factors, it is also very sensitive to traffic data (vehicle type and age mix, miles of roadway type, average speed) that are best developed by local traffic surveys. Where air quality levels are developed by a proportional or rollback model, data must be obtained on at least a countrywide basis.[19] The use of a dispersion model requires that the data be developed on a grid basis.[19] The grid size is dependent on the sophistication of the calculation; grid cells down to 1 square mile or 1 square kilometer are often used. The Chicago area transportation study[20] used traffic zones in the study area that varied from 0.25 square mile in the central business district to 36 square miles in the outlying areas. A study of Washington, D.C.,[21] divided the metropolitan area into 48 irregular subareas that were smaller in the central business district than in the suburbs. This unique approach to the evaluation of transportation alternatives provided a method for estimating emissions from transportation data without trip distribution and traffic assignment models. The method makes use of vehicle trip forecasts along with highway network information to estimate future travel, the speeds at which this travel will occur, and the emission levels produced.

Table 10-2. SAMPLE CALCULATION OF GASOLINE MOTOR VEHICLE EXHAUST EMISSION FACTORS FOR HYDROCARBONS FROM LIGHT-DUTY VEHICLES

Model year	c_i	d_i	m_i[a]	s_i	$c_i d_i m_i s_i$
1971	2.9	1.00	0.013	0.79	0.03
1970	3.6	1.05	0.075	0.79	0.22
1969	4.4	1.16	0.174	0.79	0.70
1968	4.5	1.21	0.135	0.79	0.58
1967	8.8	1.00	0.103	0.79	0.72
1966	8.8	1.00	0.115	0.79	0.80
1965	8.8	1.00	0.097	0.79	0.67
1964	8.8	1.00	0.083	0.79	0.58
1963	8.8	1.00	0.060	0.79	0.42
1962	8.8	1.00	0.059	0.79	0.41
1961	8.8	1.00	0.027	0.79	0.19
1960	8.8	1.00	0.017	0.79	0.12
1959	8.8	1.00	0.010	0.79	0.07
1958	8.8	1.00	0.032	0.79	0.22
Total					5.85

[a] See Reference 13 for sample calculation.

Table 10-3. SAMPLE CALCULATION OF WEIGHTED SPEED ADJUSTMENT FACTOR FOR HYDROCARBON EXHAUST EMISSIONS FROM LIGHT-DUTY VEHICLES

Average speed (j),[a] miles/hour	f_j[b]	v_j	$f_j v_j$
20	0.40	1.00	0.40
30	0.15	0.77	0.12
40	0.20	0.69	0.14
50	0.15	0.54	0.08
60	0.10	0.48	0.05
Total			0.79

[a] Speeds used were determined arbitrarily for purposes of this sample calculation.

[b] Determined arbitrarily.

Table 10-4. SAMPLE CALCULATION OF GASOLINE MOTOR VEHICLE CRANKCASE AND EVAPORATIVE EMISSION FACTORS FOR HYDROCARBON FROM LIGHT-DUTY VEHICLES

Model year	h_i	m_i	$h_i m_i$
1971	0.5	0.013	0.01
1970	3.0	0.075	0.22
1969	3.0	0.174	0.52
1968	3.0	0.135	0.40
1967	3.8	0.103	0.39
1966	3.8	0.115	0.44
1965	3.8	0.097	0.37
1964	3.8	0.083	0.32
1963	3.8	0.060	0.23
1962	7.1	0.059	0.42
1961	7.1	0.027	0.19
1960	7.1	0.017	0.12
1959	7.1	0.010	0.07
1958	7.1	0.032	0.23
Total			3.9

EPA's Guide for Compiling a Comprehensive Emission Inventory[22] provides detailed procedures for preparing stationary and mobile source emission inventories. The section on gasoline-powered motor vehicles is particularly useful. Although this approach requires automatic data processing equipment, it will produce a uniform format that allows ready comparison with other regions and that is compatible with stationary source data now being accumulated. This approach is recommended because of its relationship to EPA's National Environmental Emissions Data System. If the Guide is used, the gasoline-powered vehicle emission factors in Reference 1 should be used until Compilation of Air Pollutant Emission Factors[23] is revised to include them. Tables 10-5 and 10-6 present emission factors for diesel engine and aircraft emissions.

Where a detailed transportation emissions inventory, air quality data, and the necessary technical expertise are all available, rather sophisticated evaluations of transportation control and highway system alternatives are possible. Such an approach was developed by the Argonne National Laboratory.[24]

Hydrocarbon Emissions from Stationary Sources

Hydrocarbon emissions from stationary sources are estimated using emission factors. Because such emission factors may at times be based on limited or vari-

Table 10-5. EMISSION FACTORS FOR DIESEL ENGINES[a,23] EMISSION FACTOR RATING: B

Pollutant	Heavy-duty truck and bus engines		Locomotives	
	$lb/10^3$ gal.	$kg/10^3$ liters	$lb/10^3$ gal.	$kg/10^3$ liters
Particulates	13	1.56	25	3
Oxides of sulfur (SO_x as SO_2)[b]	27	3.24	65	7.8
Carbon monoxide	225	27.0	70	8.4
Hydrocarbons	37	4.44	50	6.0
Oxides of nitrogen (NO_x as NO_2)	370	44.4	75	9.0
Aldehydes (as HCHO)	3	0.36	4	0.48
Organic acids	3	0.36	7	0.84

[a] Data presented in this table are based on weighting factors applied to actual tests conducted at various load and idle conditions with an average gross vehicle weight of 30 tons (27.2 metric tons) and fuel consumption of 5.0 mi/gal. (2.2 km/liter).

[b] Data for trucks and buses based on average sulfur content of 0.20 percent, and for locomotives, on average sulfur content of 0.5 percent.

able data, emission factors should be used with caution unless the data upon which the factor is based have been studied or reviewed.

Reference 23 is a compilation of available emission factors for hydrocarbons and other pollutants from various types of sources. These emission rates are for uncontrolled sources unless otherwise noted. An example of how emission factors are used is given below:

Petroleum refinery, fluid catalytic cracking unit:

Given: Fluid catalytic cracking unit with 10,000 barrels per day of fresh feed; operates 350 days per year and has no carbon monoxide boiler.

Find: Annual hydrocarbon emissions.
Hydrocarbon emission factor (from Reference 23): 220 pounds per 1000 barrels of feed.
(10,000 bbl/day) (220 lb/1000 bbl) (350 day/year)

= 770,000 lb HC/year

Nitrogen Oxide Emissions from Stationary Sources

As in the case of hydrocarbon emissions, nitrogen oxide emissions are also estimated using emission factors. However, unlike the hydrocarbon case, development of accurate NO_x emission factors is very difficult because of the complex nature of NO_x formation from combustion processes.

Table 10-6. EMISSION FACTORS FOR AIRCRAFT[23]
(lb/engine - LTO cycle and kg/engine - LTO cycle)
EMISSION FACTOR RATING: A

Type of aircraft	Particulates		Sulfur oxides		Carbon monoxide		Hydrocarbons		Nitrogen oxides		Aldehydes	
	lb	kg	lb	kg	lb	kg	lb	kg	lb	kg	lb	kg
Turbofan												
Jumbo jet[a]	10	4.54	2	0.91	28	12.7	3	1.36	6	2.72	0.5	0.23
Long range[b]	8	3.63	2	0.91	26	11.8	17	7.7	5	2.27	0.5	0.23
Medium range[c]	7	3.18	2	0.91	16	7.3	0.6 to 86 [d]	0.27 to 39.0[d]	7	3.18	0.5	0.23
Turbojet[e]	11	5.0	2	0.91	24	10.9	26	11.8	5	2.27	1.0	0.45
Turboprop[f]	6	2.72	1	0.45	2	0.91	3	1.36	5	2.27	0.2	0.09
Turboshaft[g]	3	1.36	1	0.45	6	2.72	0.5	0.23	0.6	0.27	0.2	0.09
Piston												
Transport[h]	5	2.27	0.13	0.059	303	137.0	40	18.2	0.4	0.18	0.2	0.09
Light	0.2	0.09	0.01	0.0045	12	5.5	0.4	0.18	0.2	0.09	0.1	0.05

[a] Based on Pratt and Whitney JT-9D engine.

[b] Based on Pratt and Whitney JT-3D engine.

[c] Based on Pratt and Whitney JT-8D engine.

[d] Use 50 (22.7) for uncontrolled jets and 3 (1.36) for jets equipped with smoke burner cans.

[e] Based on General Electric CJ805-3B, Pratt and Whitney JT-3C-6, and Pratt and Whitney JT-4A engines.

[f] Based on General Motors-Allison 501-D13 engine.

[g] Based on General Electric CT 58 engine.

[h] Typical engine used is the Pratt and Whitney R-2800.

There is no convenient way of anticipating the approximate amount of NO_x pollutants formed from a given amount of fuel, as there is for the oxides of sulfur (SO_x). The formation of SO_x is directly related to the concentration of sulfur in the fuel. On the other hand, NO_x can be formed in substantial concentrations of several hundred parts per million or more with no chemically bound nitrogen in the fuel.

The amount of NO_x emitted depends upon equipment design, a complex set of combustion conditions, and operating variables such as installation size, type of burner, cooling surface area, firing rate, and air/fuel ratio. Consequently, the determination of accurate emission factors that represent average or typical emissions from each class of equipment involves a complicated sampling procedure, which requires the selection of representative operating conditions.

Reference 23 is a compilation of average emission factors for NO_x and other pollutants from various types of sources. These emission rates represent uncontrolled sources unless otherwise noted. For an operation in which control equipment is utilized, the emission rate given for an uncontrolled source must be multiplied by one minus the percent efficiency of the equipment, expressed in hundredths.

An example of how to use emission factors is given below:

Given: Power plant burns 50 million gallons of fuel oil per year.

Find: Annual NO_x emissions.

NO_x emission factor (from Reference 23): 105 pounds per 1000 gallons of fuel.

(50,000,000 gal./year)(105 lb/1000 gal.) = 5,250,000 lb NO_x/year

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CHAPTER 11

ECONOMIC CONSEQUENCES OF OXIDANT POLLUTION

COST OF OXIDANT EFFECTS

Total costs of air pollution effects consist of "damage" costs and "avoidance" costs.[1] Damage costs are those resulting directly from exposure to pollutants and include the tangible costs of medical and hospital care, costs of loss of work due to pollution-caused illness, costs of damage and/or repair of damage to materials and vegetation, and costs associated with destruction of ecosystems. Intangible costs--not easily given a dollar value--include those arising from psychological disturbances caused by the damage effects as well as by loss of aesthetic, recreational, and other environmental amenities. Avoidance costs are those caused by actions taken to avoid pollution, e.g., migration into less polluted areas. Such costs are also difficult to be given a dollar value as they are usually caused by more than one reason.

One national estimate of total air pollution damage costs, reported by the Council of Environmental Quality (CEQ), is summarized in Tables 11-1 and 11-2.[1] Such estimates are by no means complete or reliable; for example, they do not include health damage directly caused by automobile pollutants and include only one measure of the intangible costs of air pollution. Further, they disagree with other estimates. For example, Babcock and Nagda[2] reported a cost figure as high as $20 billion compared to CEQ's $16 billion. More recent estimates of the damage costs associated with individual pollutants are summarized in Table 11-3 and total as much as $8.7 billion, the oxidant contribution estimate ranges from $0.5 billion to $1.5 billion.[3]

In conclusion, EPA's best estimate of total air pollution damage cost for 1970 is $12.3 billion. EPA's best estimate of the oxidant contribution is $1.1 billion.[4]

DIRECT COSTS OF ABATEMENT

Ideally, this chapter should deal with the cost of implementing oxidant abatement policies. However, while some abatement actions are addressed directly and wholly to the photochemical oxidant problem, complete disassociation of this problem and related abatement from the other air pollution problems is extremely difficult. For this reason, the following discussion will deal first with the better established abatement cost for air pollution in its totality; estimates of the oxidant-related contribution will then be discussed.

Costs of implementing abatement policies consist of "transaction" costs and "abatement" costs,[1] and are borne partly by the public sector (Federal, state, and

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Table 11-1. ESTIMATED AIR POLLUTION DAMAGE COSTS IN THE UNITED STATES, 1968

Type of cost	Annual cost, billions of dollars
Damage costs	
Materials damage	4.8[a]
Damage to crops	0.1[b]
Cleaning of soiled materials	--[c]
Damage to human health	6.1[d]
Damage to animal health	--[c]
Reduced property values	5.2
Other	--[c]
Avoidance costs	--[c]
Total	16.2

[a] Includes damage to 50 materials thought most susceptible to air pollution deterioration.

[b] Includes direct visible effects.

[c] Not estimated.

[d] Includes estimates on treatment and prevention costs for illnesses caused by air pollution plus income lost due to morbidity and early mortality.

Table 11-2. ESTIMATED AIR POLLUTION[a] DAMAGE COSTS IN THE UNITED STATES FOR 1968 AND 1977 WITH NO POLLUTION CONTROL

Damage class	Annual cost of damage, billions of dollars	
	1968[b]	1977[c]
Health	6.1	9.3
Residential property	5.2	8.0
Materials and vegetation	4.9	7.6
Total	16.2	24.9

[a] Including oxidant, nitrogen dioxide, carbon monoxide, sulfur dioxide, and particulate matter.

[b] In 1968 dollars.

[c] In 1970 dollars.

Table 11-3. SUMMARY OF THE UNITED STATES AIR POLLUTION DAMAGE COST RANGES FOR 1970

Damage effect	Damage cost range, millions of dollars					
	Particulate matter	Sulfur dioxide	Nitrogen dioxide	Oxidants	Carbon monoxide	Total
Health	8-41	1-4	0-1	44-221	9-44	62-311
Materials	169-767	215-972	52-236	254-791	30-134	720-2900
Plants	10	4	2	116	0	132
Animals	1-3	0	0	4-11	0-2	3-16
Property values	300-1765	126-745	47-275	67-399	19-114	559-3298
Soiling	519-2077	0	0	0	0	519-2077
Visibility	0	0	0	0	0	0
Total	1007-4663	346-1725	101-514	483-1538	58-294	1995-8734

local government), and partly by the private sector (industry). Transaction costs--borne mainly by the public sector--consist of costs of research, development, planning, monitoring, and enforcement needed to achieve environmental goals and standards. Abatement costs--borne almost entirely by the private sector--are by definition those of emission reduction. It should be noted, however, that since any emission reduction activity has unavoidable side effects (e.g., effects on productivity, product quality, by-product revenue, etc.) of economic impact, the true cost of such activity cannot be given a dollar value with any confidence. For this reason, abatement costs, as estimated, can only have a gross nature.

Table 11-4 includes data on estimated transaction costs to the Federal government for 1972. It should be noted that these costs do not include those borne by state and local government and by the private sector. One estimate of the cost borne by the state and local government for 1972 is $56.8 million,[5] thus bringing the transaction costs total to $322 million.

Table 11-4. FEDERAL TRANSACTION COSTS ASSOCIATED WITH AIR POLLUTION ABATEMENT, 1972[1]

Type of cost	Cost, millions of dollars
Research and development	136.5
Planning	2.2
Monitoring and surveillance	29.0
Administration, standard setting, enforcement	82.0
Other	15.0
Total	264.9

Table 11-5 includes data on abatement costs for 1971 and, as projected, for 1981.[1] The projection data reflect not only population and human activity growth, but also planned additional controls to achieve an additional improvement of air quality.

Table 11-5. COST OF AIR POLLUTION ABATEMENT[a,1]

Cost type	Annual cost, billions of 1972 dollars 1971	1981	Cumulative 1972-1981
Public	0.2	1.2	8.4
Private			
Mobile sources[a]	1.2	10.5	58.8
Stationary sources	0.7	5.7	38.4
Total	2.1	17.4	105.6

[a]Excluding heavy-duty vehicles.

Based on the data in Tables 11-4 and 11-5, the total annual direct cost of implementing air pollution abatement policies in the United States amounts to $2.4 billion for 1972 and to $4.0 billion, approximately, for 1973.

Of this total cost for abatement, only a fraction is due to oxidant-related control. Calculation of this fraction is based on certain facts and assumptions. One fact is that oxidant abatement is pursued through unilateral control of hydrocarbon emissions. Therefore, only the cost of hydrocarbon control needs to be considered here. To calculate cost of hydrocarbon control, the approximation--a reasonable one--is made that all controllable hydrocarbon emissions are discharged from mobile sources, from storage tanks and catalyst regenerators of refineries, and from solvent evaporation. Cost estimates for control of such emissions are as follows.

No reliable estimate of the annual transaction cost of hydrocarbon control has been made; such cost must be a fraction of the $322 million estimated to be the transaction costs for all emissions.

Annual cost of control of motor vehicle emission has been estimated to be $1.0 billion for 1972, $1.9 billion for 1973, and $8.4 billion for 1977.[5] These costs include only those directly resulting from Federal requirements; costs from state activities are not included. Further, these costs are--at least for the early years in the decade of the 70's--mainly for control of carbon monoxide and hydrocarbons and only to a lesser degree for nitrogen oxide control. One way of calculating the hydrocarbon control cost portion is based on use of hardware cost data reported by the National Academy of Science, Committee on Motor Vehicle

Emissions.[3] From such data it can be estimated that the cumulative cost of hydrocarbon control hardware and maintenance for 1972 model-year autos is approximately 44 percent of the total control hardware and maintenance cost; analogous percentage figures for 1973 and 1977 models are 64 and 35 percent, respectively. Further, from data on fuel economy loss due to control, it is estimated that, for the 1972 models, 50 percent of such loss is caused by the hydrocarbon controls; analogous percentage figures for the 1973 and 1977 models are 38 and 67 percent, respectively.[5] From these estimates it can be deduced that the cost of the motor vehicle hydrocarbon emission control is roughly $0.5 billion for 1972, and $1.1 billion for 1973.

Control costs for hydrocarbon emissions from refineries--more specifically, from catalyst regenerators and storage tanks--have been estimated to amount to roughly 20 percent of the total refinery emission control cost, that is, $14.6 million per year.[5]

No reliable estimates for solvent emission control cost are available.

Based on these figures, the total hydrocarbon control cost is at least $0.5 billion for 1972, and $1.1 billion for 1973.

Estimates of annual control cost per unit are given in Tables 11-6 and 11-7 for light-duty vehicles and heavy trucks, respectively.[5] Such costs include only operating and maintenance costs and range, within the period 1968-1977, from $6.1 to $64.7 for light-duty vehicles, and from 0 to $422 for heavy-duty diesel engines. (Corresponding costs of operating a typical $3470 automobile total $2060 for the first year, and $1470 for the second. A typical heavy-duty diesel truck costs approximately $20,000.) Total cost of control hardware[3] brings the annual control cost to $67 for 1972.

Table 11-6. ANNUALIZED UNIT COST INCREASES FOR LIGHT-DUTY VEHICLES[5]
(dollars)

Cost type	Model year									
	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977
Increased fuel use				15.90	15.90	21.50	21.50	40.60	40.60	40.60
Maintenance	6.10	6.10	6.10	12.70	12.70	15.60	15.60	60.10[a]	60.40[a]	60.40[a]
Maintenance offsets								-36.30[b]	-36.30[b]	-36.30[b]
Total annual operating and maintenance	6.10	6.10	6.10	28.60	28.60	37.00	37.00	64.40	64.70	64.70

[a] Based on average of Alternative 1 for 1975-77 shown in Table 3-5.

[b] Offsets for reduced requirements for present type tune-ups and exhaust system maintenance.

Table 11-7. ANNUALIZED UNIT COST INCREASES FOR HEAVY-DUTY TRUCKS[5] (dollars)

Cost type	Model year 1968-69	1970-72	1973	1974	1975	1976	1977
Gasoline engines							
Increased fuel use[a]	None				68.40	68.40	68.40
Maintenance	None		9.90	9.90	31.70	31.70	31.70
Total operating and maintenance penalties	None		9.90	9.90	100.10	100.10	100.10
Annualized control investment costs[b]	None	1.80	8.20	8.20	48.40	48.40	48.40
Total annualized cost increase	None	1.80	18.10	18.10	148.50	148.50	148.50
Diesel engines							
Increased fuel use[c]	None		None	None	222.00	222.00	222.00
Annualized control investment costs[b]	None		None	None	200.00	200.00	200.00
Total annualized cost increase	None		None	None	422.00	422.00	422.00

[a] Based on average of 1380 gal. of fuel per year as baseline, fuel at 33¢/gal.

[b] Based on 5-year engine life, annualized straight-line basis.

[c] Based on average of 10,660 gal. of fuel per year as baseline, fuel at 26¢/gal.

Total increase in emission control hardware price from an uncontrolled 1968 automobile to a 1976 dual-catalyst system (needed to meet the 1977 model-year standards) controlled automobile has been calculated by the National Academy of Sciences to be $373 per automobile; EPA predicts $327.50; industry estimates range from $298 to $428.[3] Operating and maintenance costs (Tables 11-6 and 11-7) raise this per unit cost by another $260.

The per unit costs reported here are for control of carbon monoxide, hydrocarbon, and nitrogen oxide emissions. The cost of the hydrocarbon control alone can be calculated, as mentioned earlier, based on the control hardware cost data reported by the National Academy of Science,[3] and on maintenance and fuel cost data reported by EPA (see Table 11-6).[5] In these calculations, hardware needed for hydrocarbon control was differentiated from hardware needed for carbon monoxide and nitrogen oxide control, and total hardware and maintenance costs were broken down accordingly. Also, fuel economy loss due to hydrocarbon controls was taken to be 50 percent of the loss due to all controls for the 1971-1972 models, 58 percent for the 1973-1974 models, and 67 percent for the 1975 models (before the 1-year extension of the emission standards was granted). Based on these data and assumptions, the annual cumulative per-auto costs of hydrocarbon emission control in the United States were estimated and are given in Table 11-8.

Table 11-8. ESTIMATES OF ANNUAL (CUMULATIVE) UNIT COSTS OF LIGHT-DUTY MOTOR VEHICLE HYDROCARBON EMISSION CONTROL[a]
(1972 dollars)

	Model year								
Cost type	1968	1969	1970	1971	1972	1973	1974	1975	1976
Hardware	14.25	14.25	16.60	16.60	16.60	60.90	71.73	130.90	130.90
Increased fuel consumption	0	0	0	7.95	8.10	8.10	8.10	27.00	27.00
Maintenance	6.10	6.10	4.60	9.58	6.00	10.25	9.93	7.43	8.50
Total	20.35	20.35	21.20	34.13	30.55	79.25	89.76	165.33	166.40

[a] Estimates are for control systems designed to meet the set of emission standards in effect in 1972 and based on catalytic oxidation of exhaust hydrocarbons.

IMPACT OF ABATEMENT ON ECONOMY

The desirable and intended impact of control is to reduce pollution costs. Such tradeoffs between damage costs and abatement costs are illustrated by the data of Table 11-9, which summarizes the original estimates of costs associated with implementing the Clean Air Act of 1970.[1] Based on the incomplete data available, total damage costs of air pollution in 1977 with no controls are expected to be about $25 billion. With controls, damages are estimated at $11 billion, and abatement costs are $12 billion, resulting thus in savings of $2 billion. From the data of Table 11-9, it appears that mobile source emission controls are not cost effective. This tradeoff estimate, however, is inaccurate since the damage costs do not include many of the damages resulting from the primary auto emissions (carbon monoxide, nitrogen oxides, and hydrocarbons).

Table 11-9. ESTIMATED COST EFFECTS OF THE CLEAN AIR ACT FOR FISCAL YEAR 1977[1]
(billions of 1970 dollars)

Emission source	Damage costs		Control costs
	Without controls	With controls	
Mobile	2.2[a]	1.2[a]	8.4
Stationary fuel consumption	12.8	3.4	2.5
Industrial processes	7.0	3.7	1.2
Miscellaneous	2.3	2.3	0
Total	24.3	10.6	12.1

[a] Health damage costs from carbon monoxide, nitrogen oxide, and hydrocarbon emissions are not included due to lack of data.

Beyond the initial cost effect of air pollution abatement are the secondary impacts that spread into other sectors of the economy. Such impacts have both negative and positive effects. Thus, abatement costs raise the prices of pollution-causing articles and services, thus reducing sales of such articles and services--a negative effect. On the positive side, the demand for pollution abatement equipment induces new investment and higher employment, thus creating higher income and more spending. The Council on Environmental Quality, the Environmental Protection Agency, and the Commerce Department have made several attempts to quantify these impacts of pollution control throughout the entire economy. First results showed that the overall impact on the economy was minor.[6]

Another impact of control is on energy consumption. The emission control methods presently used by the U.S. automobile manufacturers have caused an increase in fuel consumption of 7 to 15 percent. However, it is not certain whether present fuel penalties will continue with emission control technology now being developed for future use.

Finally, it is expected that the emission standards and control actions will have an impact on the balance of international trade. Initial studies indicated a maximum negative impact on U.S. net exports between $2 billion and $3 billion during the peak years of 1975 and 1976.[6] However, these projections are clearly overestimated because the economic model used made no allowances for foreign pollution abatement regulations. Other estimates indicate the U.S. net exports to rise slightly in spite of increased pollution control costs.[7] Overall, the information available is not sufficiently complete to permit a reliable estimation of pollution abatement effects on international trade.

REFERENCES FOR CHAPTER 11

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